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# "Ionic conductivity of ion-exchange membranes used as solid electrolyte in fuel cells: Influence of the salts"

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# ABSTRACT

In this work, the ionic conductivity was determined by complex impedance spectroscopy in aqueous solution of two groups of membranes in order to characterize their electrochemical properties. The contributions of the membranes as well as the influence of the electrolyte solutions in the system have been evaluated. Thus, two different types of membranes were studied: proton exchange membranes (PEMs) and anion exchange membranes (AEMs), respectively. In the case of PEMs, novel membranes alternative to Nafion were used. These membranes are based on multiblock copolymers (SPES) and three different samples (3, 6 & 9) were studied. In AEMs, a semi-interpenetrating network membrane composed by polysulfone has been used. Different electrolyte solutions such as $NaCl, HCl, KCl\ and\ NH_4Cl$ in the case of PEMs, and $NaCl, KCl, KOH\ and\ NH_4Cl$ in the case of AEM ones have been used.

The measurements have been done in a homemade cell using $Ag/AgCl$ as reference electrodes and graphite as electrode work. For all the electrolytes and membranes conductivity studies, the admittance and the impedance have been studied using different diagrams like Nyquist or Bode.

In order to compare and examine the conductivity results, many factors such as the ion mobility, ionic dissociation group or number of functional groups have been taken into account to obtain the more precisely information from all the electrolytes and membranes.

The ionic conductivity of the membranes varied as a function of the concentration of the electrolytes as well as the number of functional groups in the polymeric backbones. PEMs and AEMs showed a good chemical stability and high conductivity values essential to be proposed as solid electrolytes membranes in fuel cells.

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# 1. INTRODUCTION

## 1.1 Fuel cells and environment

During the last century, an increment on the combustion of fossil fuels has taken place. This action, mainly used for the generation and transportation of energy, has two main problems such as severe future impact in the economy, because it is produced from finite resources, and the release of different pollutants to the atmosphere such as gaseous ($SO_2$, $CO$ ...), persistent organic (pesticides, dioxins…), heavy metals (vanadium, manganese, cadmium…) and particulate matter contaminating the air, what also produces the pollution of foods and water, causing several illness like cancer, birth defects, difficulty in breathing… as much in humans as in animals. [1]

Due to these problems, since many years ago, scientists have been looking for a reliable alternative of fossil fuels, less polluting and with the same efficiency. At that point, hydrogen has been an attractive alternative, due to that fact that it can be obtained from different resources, renewable or non-renewable, in a sustainable way reducing $CO_2$ emissions, enhancing the air quality, creating a new industrial energy with an economic prosperity and guarantying security of energy supply. Moreover it has more applications than fossil fuels since it is versatile, it can be domestically produced, its combustion does not emit $CO, SO_2$ ... and it allows the possibility of storing energy. For that reason, hydrogen is already made in different industries and in huge volumes, being the fuel cells one of its most important uses in terms of high-efficiency for transportation and generation of electricity. [2]

A fuel cell is a device, similar to a battery, in which electrochemical reactions produce energy. [3] The main difference between a battery and a fuel cell is that the first one allows storing energy while the other may not store energy but produce electrical energy if fuel is supply. [4] The first references to hydrogen fuel cells appeared in 1838 when, the Welsh judge and physical scientist, William Grove discovered that joining one side of the two platinum electrodes in a sulfuric acid container, and the other side in containers separately sealed of oxygen and hydrogen, what is the same of reversing the electrolysis process, water and electricity could be produced. This discovery gave the opportunity to take an alternative way from the fossil fuels. [5]

Since that moment until nowadays, many advantages of the fuel cells over the conventional power sources have been discovered, such as longer useful life, relative safety, zero toxicity, minimal maintenance cost, less dependence on fossil fuels…, and taking also into account that they are more efficient in extracting energy from a fuel than combustion processes, they have been applied in many different gadgets and systems like in small stationary power generators between 0.5 to 10 kW and in the batteries of portable devices, smart-phones, PCs, … [6]

There are several types of fuel cells and each one has different applications. These differentiations are because of three reasons: the operation temperature, the type of ion that is transferred and type of electrolyte.

Normally, the classification used is the one determined by the type of the electrolyte, which is represented on the following table 1.

**Table 1.** Advantages and applications of the different fuel cells [7]

| Fuel Cell Type | Common Electrolyte | Operating Temperature | Typical Stack Size | Efficiency | Applications | Advantages | Challenges |
|---|---|---|---|---|---|---|---|
| Polymer Electrolyte Membrane (PEM)* | Perfluoro sulfonic acid | 50-100°C 122-212°F | 1 kW-250 kW | 60% transportation 35% stationary | • Backup power • Portable power • Distributed generation • Transportation • Specialty vehicles | • Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up | • Expensive catalysts • Sensitive to fuel impurities |
| Alkaline (AFC) | Aqueous solution of potassium hydroxide soaked in a matrix | 90-100°C 19-212°F | 10-100 kW | 60% | • Military • Space | • Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components | • Sensitive to $CO_2$ in fuel and air • Electrolyte management |
| Phosphoric Acid (PAFC) | Phosphoric acid soaked in a matrix | 150-200°C 302-392°F | 400 kW 100 kW module | 40% | • Distributed generation | • Higher temperature enables CHP • Increased tolerance to fuel impurities | • Pt catalyst • Long start up time • S sensitivity |
| Molten Carbonate (MCFC) | Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix | 600-700°C 1112-1292°F | 300 kW-3 MW 300 kW module | 50-60% | • Electric utility • Distributed generation | • High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP | • High temperature corrosion and breakdown of cell components • Long start up time • Low power density |
| Solid Oxide (SOFC) | Yttria stabilized zirconia | 600-1000°C 1112-1832°F | 1 kW-2 MW | 50-60% | • Auxiliary power • Electric utility • Distributed generation | • High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle | • High temperature corrosion and breakdown of cell components • HT operation requires long start up time and limits shutdowns |

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 250 W and operating at 60-90°C.

Although, as mentioned before, there are different fuel cell types and everyone operates a bit different, all of them have two electrodes (anode and cathode) and an electrolyte, and follow an electrochemical process where a redox reaction takes place. In that process, as it can be observed in Figure 1, the anode (which is positively charged) transfer electrons to the cathode (which is negatively charged) by means of an oxidation reaction that, by a reduction reaction, gain those electrons. This procedure makes possible to generate electricity converting chemical energy into electrical one. [3]

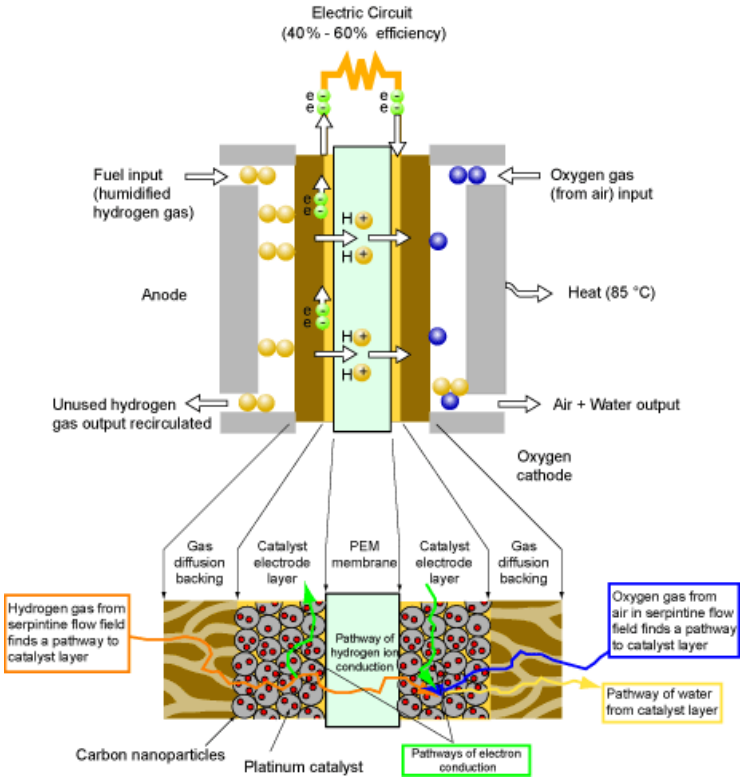


**Fig. 1:** Electric circuit in a fuel cell [8]

The redox reaction that takes place on the fuel cells is the following: [9]

Oxidation process produced on the anode:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (2.1)$$

Reduction process produced on the cathode:

$$\frac{1}{2}O_2 + 2H^+ \rightarrow H_2O \qquad (2.2)$$

Total exothermic reaction:

$$\frac{1}{2}O_2 + H_2 \rightarrow H_2O \qquad (2.3)$$

In the most common fuel cells, Hydrogen is the basic fuel element, although Oxygen is also required. This kind of fuel cells are known as proton exchange membrane fuel cells (PEMFCs), which is one of the types of solid electrolyte fuel cells and it is the one we are going to study on the following points.

We will also analyze an alternative from the PEMFCs, which are the anion exchange membrane fuel cells (AEMFCs). This kind of fuel cells, instead of moving a proton, $H^+$, from the anode to the cathode, moves an anion, $OH^-$ or $Cl^-$, in that sense.

## 1.2 Proton exchange membrane fuel cells (PEMFCs)

Proton-exchange membrane fuel cells are a type of fuel cell that use polymer electrolyte membranes to conduct protons for ion exchange goals. In order to complete that process, the hydrogen, typical fuel used, is sent to a positive electrode called anode. There, the catalyst oxidizes the fuel and divide it into negative and positive ions, passing the electrons through the external circuit from the anode to the cathode converting the resulting current into useful power, while the protons (positive ions) pass through the electrolyte membrane towards the cathode where it combines with the electrons and react with oxygen to create water. [9]

PEMFC have recently attracted much attention from both a fundamental and an applied point of view for their future potential as clean and mobile power sources. Although in 1960s, NASA implemented for the first time in the Gemini spacecraft to supply electricity and drinking water to the astronauts from the hydrogen and oxygen available in the tank, the high cost of the catalysts and the several difficulties of management produced a standstill in the development of PEMFC, not being until 1990s when the implementation of a reliable polymer electrolyte membrane configuration and a reduction in the production expenses of some catalysts, such as the alkaline ones, provoked a huge reduction on the total cost. Creating again an interest in this kind of fuel cells what produced new developments and studies. [10]

Although it still needs more investigation mainly to reduce the costs in some parts of the fuel cell, such as most of the catalyst or to improve the efficiency, it is already used in several applications like in the area of transports, as energy source for vehicles, mobile power sources and portable and stationary fuel cell applications. Some of the devices where PEMFCs are applied have been shown in figure 2.


**Fig. 2:** PEMFC applications [11]

The main characteristics of PEMFC are the operational temperature, which is lower than 100˚C and produces a fast and easy start-up in comparison with the rest of fuel cells, the huge amount of energy generated in terms of volume and weight unity and it high energy density what makes them very light and compact. Other advantages that can be taken into account are: it reduction in cost because as it uses a solid electrolyte instead of a liquid electrolyte, as the most of the fuel cells does, the hermetically seal of the anode and cathode gases are more simple and provoke fewer cost in the fabrication process, and the cell has a higher lifespan due to the solid electrolyte has less corrosion problems. [9]

One of the most important components of the fuel cell is the electrolyte membrane, because it plays an important role, due to the fact that it allows the correct circulation of ions among anode and cathode and interrupts the chemical reaction if electrons or other substances travel through it. Therefore, in order to satisfy all of these characteristics, the electrodes normally used are the gas diffuser ones, which fabrication is really complicated, to guarantee the conduction where the catalysts are in contact with the ionic or electric conductor. Also, the material of the proton exchange membrane (PEM) has to be insulated, impermeable and with high conductivity. Since 1960's, the electrolyte used in this kind of fuel cells is called Nafion. [9]

## 1.3 Nafion: Chemical structure and properties

Nafion is the main synthetic polymer utilized as electrolyte in the proton exchange membrane fuel cells (PEMFC), developed and produced by E.I. DuPont Company over 1960's. It was the first ionomer, polymers made with ionic properties, creating a new class of polymers. [12]

Nafion's membrane is classified inside of the fluoropolymer's group, where fluorine is the main component and its small size and high electronegativity is what gives strength to the C-F bond. Its chemical structure (Figure 3) is formed by a main polymeric chain of polytetrafluoroethylene (PTFE) which is in charge of the mechanical stability. Side chains are joined by both bonds and sulfonic groups that are the responsible of the ionic transport. [9]

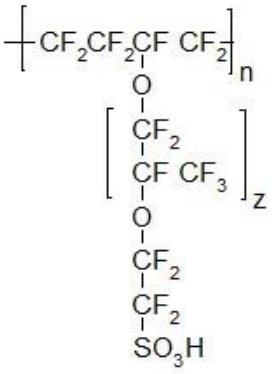


**Fig. 3:** Nafion structure

Nafion has many good physical and chemical properties, obtained by introducing in the bulk polymer matrix groups of sulfonic acid. It is an extraordinary resistant material in chemical terms, due to it does not deliver fragments into the neighboring medium. It is also highly ion-conductive, because it is a polymer that works as a cation exchanger. Another important property is that it is permeable to water, and this happens because the interconnections among Nafion's sulfonic acid groups make the water to go very fast through Nafion's membrane, making Nafion a very efficient polymer when absorbing water due to that reason it has a high water moisturize. [12]

In addition of all the previous properties, it also has a good thermal stability, high ionic exchange capacity (0.91 meq $H^+$/g), high acidity and, talking in chemistry terms, is inert. Moreover, it gets the best conductivity state at temperatures lower than 100˚C (99mS/cm), what explains why it is one of the most used membranes for PEMFC's, due to the operational temperatures of these kind of fuel cells is normally below 100˚C. [9]

The addition of sulfonic acid groups into the greater part of the polymer matrix, is what allow Nafion to have all these incredible ionic properties. This synthetic polymer is used in several applications such as the fabrication of ion-exchange membranes, to produce sodium hydroxide and chlorine gas, in the respiratory care or in the drying or humidifying breath for anesthesia, because it is a good gas dryer and humidifier. It is also used in the production of fine chemicals, as a super-acid catalyst, or in polymer electrode fuel cells as a proton exchange membrane. [12]

But in spite of all these advantages and applications, it still has some difficulties such as the cost, because it is very expensive in compare with other, the few mechanical properties it has and its low stability in temperatures higher than 100˚C. What has stimulated some new researches in new materials in order to prevent the Nafion deficits. [9]

## 1.4 Nafion alternatives: PEM composed of multiblock copolymers based on polysulfone

As mentioned on the previous point, Nafion has some disadvantages. It has produced the necessity or at least the willfulness to research about some alternatives in order to find a more efficient structure. These alternatives revolve around other polymer chains in order to use them as an electrolyte. Among these alternatives we have focused in a particular polymer called polysulfone.

### 1.4.1 Polysulfone

Polysulfone is a kind of polymer normally obtained by Friedel-Crafts condensation of sulfonyl chlorides. The polysulfone's family is made up of three different commercial types knowns as Udel, Radel and Victrex (Figure 4). These polymers are amorphous thermoplastics with a high dimensional stability, being the first one the most used in engineering terms and, therefore, the one I will focused in the following lines. [13]

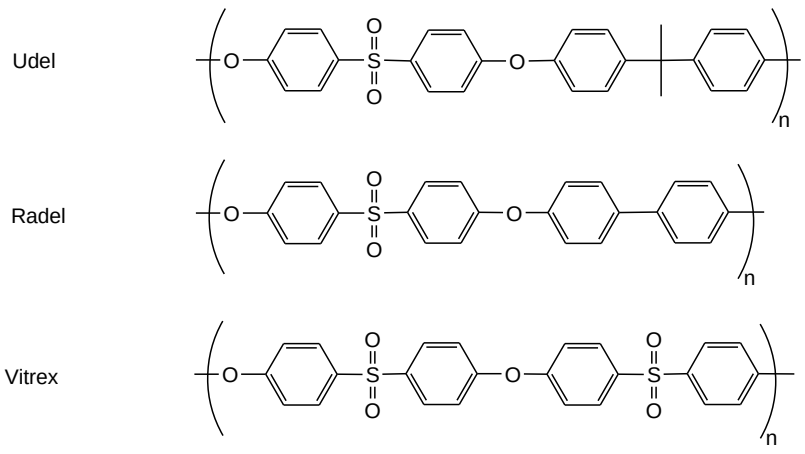


**Fig. 4:** Main polysulfone structures

The polymerization reaction of Udel is prepared from 2,2-bis(4-hydroxyphenyl) propane and 4,4-dichloro diphenyl sulphone, and takes place in dimethylformamide (DMF), that is a polar aprotic solvent. Its main characteristics are the high glass transition temperature, its high thermal stability, its excellent mechanical properties and its high chemical and oxidation resistance. It was first time commercialized in 1965 by Union Carbide Corporation and since then it has been used in several applications such as separation of gases, hemodialysis, electronic industry and in the recuperation of sewage water. [9]

The characteristic that gives these properties to the polymeric chain is the diphenyl sulfone unit, because the sulfur atom is in high oxidation state (+6) and, besides, the sulfone group try to gain electrons from rings next to it, making them poor in electrons. Therefore, the entire diphenyl sulfone unit is in an oxidation resistant state, making Udel a polysulfone with a high oxidation resistance. [13]

Also, the strength of the chemical bonds gives thermal stability to the polymer. This group has a high resonance grade, due to the groups it is composed. The output of that resonance is that the atoms fix in a rigid spatial configuration, and so that is why the diphenyl sulfone group gives to the polymer several inherent configurations such as: resistance against oxidation and rigidity even at high temperatures and thermal stability. [9]

### 1.4.2 Multiblock copolymers based on polysulfone

Polysulfone membranes have been extensively studied for PEMFC. [14] Sulfonated reaction is usually carried out in order to obtain functionalized polysulfones adding sulfonic groups in the chains. [15] The main disadvantage of this type of membrane is the low mechanical properties as well as the lost in the conductivity due to the high solubility of these sulfonic groups.

In this scenario, the search for structures that improve this problem is crucial. We have decided to first prepare a polycondensated multiblock copolymer based on Udel® and Radel® structures, and then to functionalize exclusively, or if not preferentially one of them (Fig. 5).

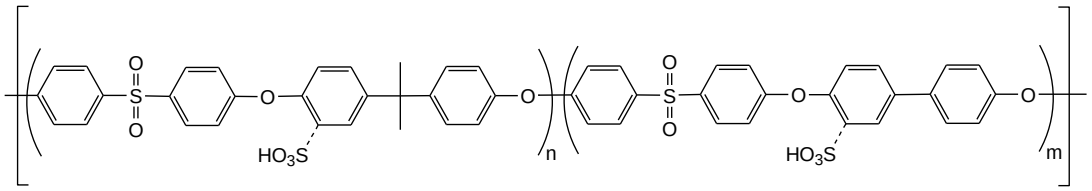


**Fig. 5:** Multiblock copolymer SPES

The multiblock copolymers show a higher proton conductivity and greater dimensional stability due to the different hydrophobic and hydrophobic phases interconnected with each other generating ionic conduction channels. [16]

## 1.5 Anion exchange membrane fuel cells (AEMFCs)

Anion exchange membrane (AEM) is a semipermeable membrane used to lead impermeable anions to gases such as oxygen or hydrogen. It is used in electrolytic and fuel cells while the anions are transported to separate the reactants around the two electrodes. This type of membrane was at the beginning of the 20th century use in the alkaline anion exchange membrane fuel cells (AAEMFCs) or anion exchange membrane fuel cells (AEMFCs). [17]

Alkaline fuel cells (AFCs) were first developed in the 1930s by F.T. Bacon, and in that time it operated with $H_2$ as the fuel among 50 and 200˚C of temperature employing a liquid electrolyte. Later, in 1960s NASA used to power Apollo space missions. Nowadays, anion exchange membrane fuel cells have been one of the main environmental sustainable energy technology studied. Researchers have focused on the polymeric anion exchange membranes (AEMs), which contains positive ionic groups and mobile negatively charged anions, due to that reason in this hydroxide transport medium cationic moieties are fixed to polymer chains preventing the formation of carbonate precipitates what block pores and mechanically disrupt and destroy active layers, and which was one of the main problems of the studies during the 20th century. [18]

Another important aspect that should be indicated is that in AEMFCs, water and ions are transported in a different direction as PEMFCs. In AEMFCs case, the water is created at the anode and at the same time it is a reactant at the cathode. This characteristic and the high alkaline medium gives AEMFCs distinction from other kind of fuel cells. [19]

Anyway, although AEMs have helped to solve some problems mentioned before and it is the key to the successful implementation of AMFCs, it still has some difficulties such as low ionic conductivity and poor chemical stability, especially at the carbonic site. If we compare the conductivity of PEMs with the AEMs there is huge difference, this is because the diffusion coefficient of $H^+$is much higher than the diffusion coefficient of $OH^-$, due to the size of the second one is greater than the first one, and this implies lower velocity of ion movement and therefore, lower conductivity.

The attention AEMFCs are receiving in recent years is principally due to the several advantages they have versus traditional proton exchange membrane fuel cells (PEMFCs), such as the use of nonprecious-metal-based electro-catalysts such as silver,

cobalt or nickel to replace expensive platinum-based its high durability or the improvement of the reaction kinetics. [20]

For the different reasons previously mentioned, AEMs are, among all known conventional hydrogen-oxygen operable fuel cells the best performing at temperatures below 200˚C.

In the following picture (figure 6) it is shown how an AEMFC works with the direction of the air and water and the different reactions that take place in the anode and the cathode.

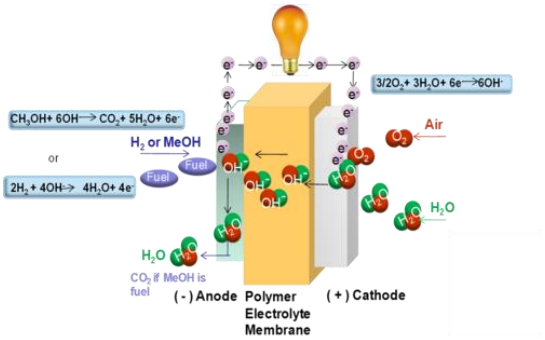


**Fig. 6:** Anion exchange membrane [21]

The associated fuel cell reactions both for a traditional AFC and also for an AMFC are: [20]

Oxidation process produced on the anode:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad (2.4)$$

Reduction process produced on the cathode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2.5)$$

Overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \quad (2.6)$$

## 1.6 Selemion & Semi Interprenetrating Networks

One of the most important anion-exchange polymer membranes, in commercial terms, is the so called Selemion. It contains $SO_3H$ groups, and it is silver-plated on the top and bottom surface. This silver compound in contact with the oxygen ($O_2$) form $Ag_2O$, and it is this redox reaction what gives to Selemion the incredible bending controllability it has. [22]

The chemical structure (figure 7) is divided in two different components. In one hand it is formed by a functionalized polystyrene copolymer that is the responsible for the properties related with the electrical issues. In the other hand, it is composed by PVC that is responsible for the mechanical properties of the material. [23]

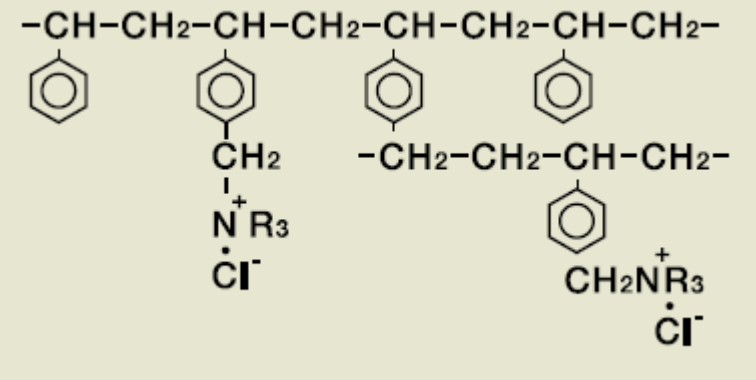


**Fig. 7:** Selemion structure [24]

In alkaline anion exchange membrane fuel cells (AAEMFCs), Selemion is the main material used as a membrane, what has helped to make these fuel cells a good cheap alternative against the PEMFCs.

One of the disadvantages of this membrane is that the PVC, one of the components that form Selemion's membrane, degrades during anion-exchange process what produces a reduction of the storage modulus. Because of this reason, some alternatives have been developed being one of these strategies the interpenetrating polymer networks. [23]

Interpenetrating polymer network (IPN) is a kind of polymer composed of two different homogeneous chemically network structures. In this case, we are going to focus on the semi-interpenetrating network for anion exchange membranes (SIPN AEMs), which is composed by one network and one linear or branched polymer. [25]

The reason we focus on SIPN AEMs is because it shows higher conductivities and better mechanical and thermal properties. [26] In this work, a SIPN membrane was used. Their chemical structure is shown in Figure 8. Polysulfone which was used as a linear polymer (thermoplastic polymer) was homogeneously dispersed within a covalently crosslinked polymer where trimethylammonium acts as a functional group and TMEDA as a crosslinking agent. The use of the same polymer for both segments (crosslinked and free polymers) is expected to improve the compatibility of the blend. So, these membranes combine the advantages of SIPN structure (improves the hydroxide conductivity maintained the dimensional and mechanical stability) and crosslinking process (enhances the dimensional stability of the membrane).

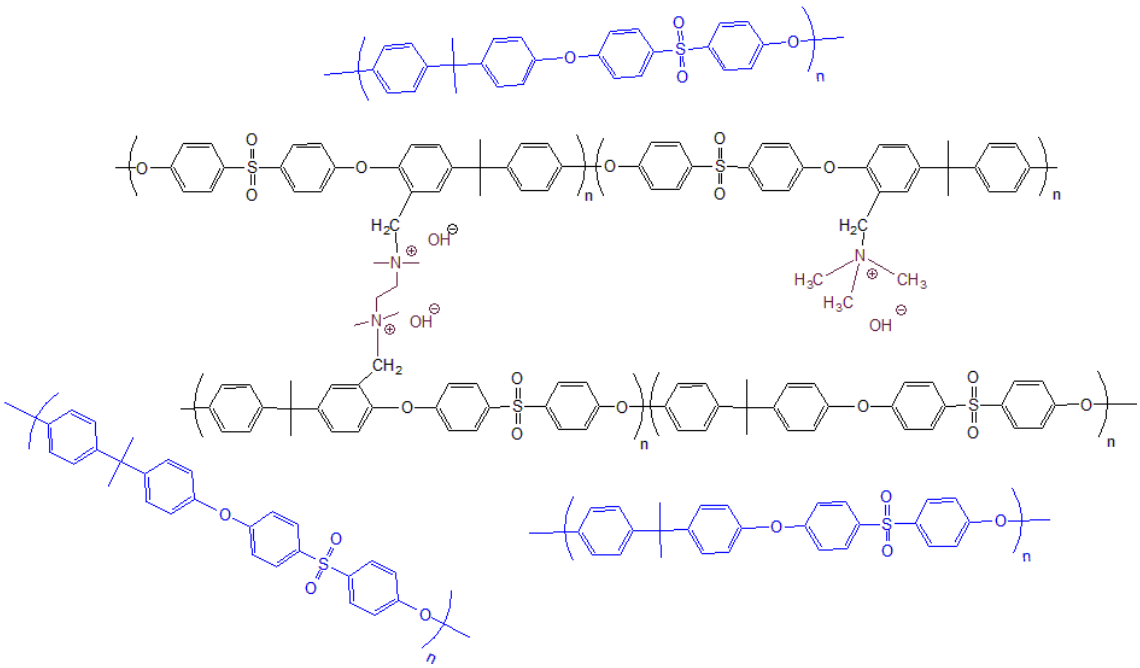

**Fig. 8:** SIPN structure

## 1.7 Transport mechanisms: Vehicular & Grotthuss

The conductivity either in proton or anion exchange membranes is the key to get good performances in the fuel cells. Therefore, a high conductivity is essential in order to obtain a high current density and it is one of the first characteristics analyzed when the membranes are studied for their use.

In the case of proton exchange membranes, the efficiency of the membrane is close related with the proton conductivity, which is one the most important characteristics

studied when choosing a membrane to be used, that at the same time has a relationship with its humidity. Therefore, when the humidity is higher, greater is the conductivity of the membrane. [9]

When talking about anion exchange membranes, at the beginning the conductivity of these kind of membranes were not as good as the proton one, but after many studies and developments in anion conducting polymers, the conductivity of these membranes have reached very similar levels as the proton exchange membranes, being also the peak power density and the limiting current density two of the main indicators of the conductivity of the membrane. When higher they are, higher is the conductivity. [19]

Other studies have also shown that AEMs have a higher free energy barrier for proton transfer reactions than PEMs, because the excess charge is less delocalized in the first ones.

In molecular terms, there are two main transport mechanisms, which are called vehicular and Grotthuss (Figures 9 & 10).

Grotthuss mechanism consists in protons, in the case of PEMs, or hydroxide ions, in the case of AEMs, tunnel from one hydrolyzed ion site to another through the whole membrane. The ion produced by oxidation in the anode adhered to the water molecule to create provisionally an ion of $H_3O^+$ and another proton coming from the same ion $H_3O^+$ goes to another water molecule. [9]

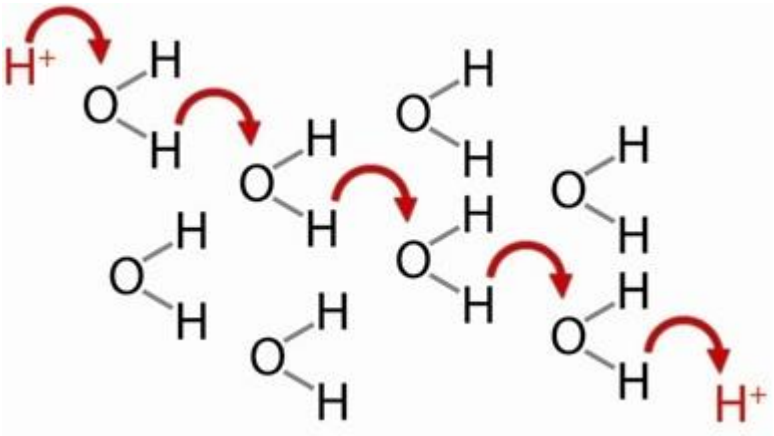


**Fig. 9:** Grotthuss mechanism [27]

This process is very similar as auto-dissociation, which is the mechanism whereby the ions ($H^+, OH^-$) initially separate. Grotthuss mechanism is more efficient with hydroxide anions, AEMs, than with protons, PEMs. [28]

Vehicular mechanism, figure 8, is based on the diffusion of the ion with the water molecules forming complex structures such as $H_3O^+$ *or* $H_5O_2^+$, through the membrane. The best property of this mechanism is the existence of free volumes inside the chains

that allow the transfer of hydrous ions through the membrane. This mechanism, unlike Grotthuss one, fits better with protons, PEMS, than with hydroxide ions, AEMS. [29]

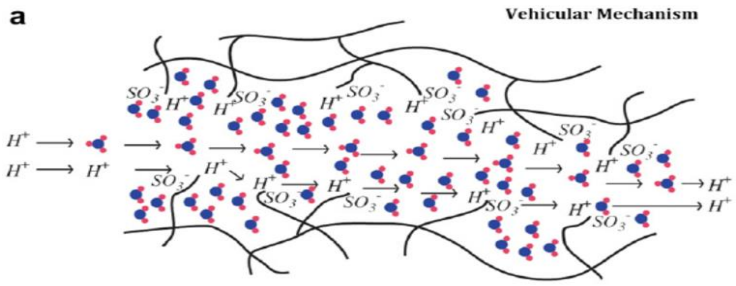


**Fig. 10:** Vehicular mechanism [30]

The main mechanism of the membranes is determined by its hydration level and by the active energy on the process. For Grotthuss mechanism, this activation energy is among 14 and 40 kJ/mol. However, for vehicular mechanism the activation energy is lower. [9]

As $H^+$ molecule is smaller than $OH^-$, the activation energy needed is lower. Due to that reason, Vehicular mechanism is more related with PEMS and Grotthuss mechanism with AEMS.

## 1.8 Conductivity of ion through exchange membrane

The conductivity of the different ions can be determined by different characteristics, what explain that although some compounds have the same anion or proton, the conductivity between them is very disparate.

One of the main aspects to take into account when analyzing the conductivity is the ion mobility, which is the ability of charged particles to move through a solution. This property is defined by the following equation:

$$u = \frac{e|z|}{6\pi\eta a} \qquad (2.7)$$

which is form by, $a$, the radius of the ion, $\eta$, the viscosity of the solution, z, the charge number of ions and ,e, the elementary charge. [31]

If we compare the cation mobility of the $H^+$, $u = 36.23 * 10^{-8} \frac{m^2}{s*V}$, with the anion mobility of the $OH^-$, $u = 20.64 * 10^{-8} \frac{m^2}{s*V}$, it can be observed than the first one is greater than the second one. The main reason of that fact is that the cation size is smaller than anion size, and that produce that the $H^+$ moves faster than the $OH^-$ what has a direct relationship with the conductivity. [31]

Another important aspect is the dissociation of the cationic or anion group. In our study, the protonic electrolytes chosen have been $NaCl, HCl, KCl \; and \; NH_4Cl$, therefore, as the anion group, $Cl^-$, is the same for all of them, its conductivity is mainly defined by their cation mobility. But, on the other hand, the anion electrolytes chosen have been $KOH, KCl, NaCl \; and \; NH_4Cl$, and as it can be observed, the cation groups are different, $K^+$, $Na^+$ and ${NH_4}^+$, so that is why in this case the conductivity is mainly defined by two aspects: the anion mobility and, unlike protonic electrolytes, the dissociation of the cationic group. When higher the dissociation, higher the ion mobility and, therefore, greater the conductivity.

In addition to the ion mobility and the dissociation of the ionic groups, the ion size is also very important for the conductivity. Because, as mentioned before, when the ion size increases, the conductivity decreases.

In order to improve the ionic conductivity, several factors, in addition to those previously explained, have to be taken into account. Thus, the polymer structure as well as the chemical, thermal and electrochemical stability plays an important role. [32]

# 2. OBJECTIVES

The present work is focused on the study of the electrochemical properties of the membranes for PEMFC and AEMFC applications. The characterization by complex spectroscopy impedance was carried out taking into account these goals:

- Complete study of the conductivity using different salts.
- Examination of the conductivity at different concentrations of the electrolytes.
- Research of the influence of the different salts in proton and anion exchange membranes.
- Study of the variation of the amount of functional groups in the polymeric structure of the proton exchange membranes and its influence on the ionic conductivity.

# 3. EXPERIMENTAL

In the following lines the laboratory procedure will be explain, such as the previous treatment of the different membranes or the materials and devices used in order to obtain the experimental results.

## 3.1 Synthesis of functionalized polysulfones & materials

The membranes used in the experimental studies have been synthesized in the doctoral thesis *"Síntesis y caracterización de membranas poliméricas conductoras iónicas para su aplicación en pilas de combustible poliméricas"* (figure 11).


**Fig. 11:** Synthesized membrane

In the case of PEMFC synthesis, the reagents employed to obtain the SPES membranes are N,N-Dimethylacetamide (DMAc, 99.0 %) and potassium carbonate ($K_2CO_3$, ≥ 99.0 %) which were purchased from Acros Organics. Trimethylsilyl chlorosulfonate (TMSCS, 99.0 %), 1,2-dichloroethane (DCE, 98.9 %) and toluene (99.8 %) were supplied by Sigma-Aldrich. 4,4'-Difluoro-diphenylsulfone (DFDPS), 4,4'-

isopropylidenediphenol (BPA), 4,4'-dihydroxybiphenyl (BP), 4,4'-dihydroxydiphenylsulfone (DHDPS), which were purchased from Alfa Aesar.

For the synthesis of AEMFC, polysulfone, tin (IV) chloride (99.0%), paraformaldehyde (95.0-100.5%), chlorotrimethylsilane (≥ 98.0%), 1-methyl-2-pyrrolidone (NMP) (ACS reagent, ≥ 99%), N, N, N′, N′-tetramethylethylenediamine (TMEDA) (≥99.5%), and trimethylamine solution (25 wt. % in H2O) were purchased from Sigma-Aldrich.

The electrochemical measurements were performed in different electrolytes (HCl, 37.0 %, KOH ≥ 85.0 %, KCl ≥ 99.0 %, NaCl, ≥ 99.5 % and $NH_4Cl$, ≥ 99.5 %) which were purchased from Sigma-Aldrich. Prior to testing the membranes, the samples were immersed in the 1 M electrolyte solution corresponding the each conductivity study for 24 h.

## 3.2 Ionic conductivity: Measurements in aqueous solutions

The ionic conductivity of the membranes was measured by means of Electrochemical Impedance Spectroscopy (EIS). This method is based on the study of the answer provoked by the application of an alternating current signal to an electrode. The devices utilized in order to measure the conductivity were an impedance analyzer Solartron 1260 connected with an electrochemical interphase Solartron 1287 (figure 12). The ranges of frequencies used were from $10^{-1}$ to $10^{6}$ Hz and the amplitude of the voltage applied was 10 mV.


**Fig. 12:** Solartron 1260 & 1287

The table 2 shows the measurement conditions such as the AC amplitude or the range of frequencies among the Solartron devices can measure.

The ionic conductivity can be evaluated by several ways, over the surface or through the membrane, with two or four electrode tips and measured in liquid or dry. [9] And it is calculated following this formula:

$$\sigma_m = \frac{L}{R_m * A} \tag{4.1}$$

where L corresponds to the thickness, $R_m$ to the resistance and A to the area of the membrane. [33]

In our case, the method chosen was through the membrane, with four electrode tips and in liquid, therefore the membrane is sunk in a solution during the measurements. In this method electrodes of $Ag/AgCl$ were used as reference electrodes, graphite as electrodes work (figure 13) and, in the case of proton membrane, a solution of $KCl$, $NaCl$, $HCl$ and $NH_4Cl$ as electrolytes with membranes of different thickness SPES3, SPES6 and SPES9. In the anion exchange membrane case, the solutions applied as electrolytes were $NaCl$, $KCl$, $KOH$ and $NH_4Cl$. For both cases, the concentrations taken were $10^{-4}, 4*10^{-4}, 10^{-3}, 4*10^{-3}, 10^{-2}, 4*10^{-2}$, $10^{-1}$, and the fuel cell is composed by two different chambers between which the membrane is located.

**Table 2.** Measurement conditions Solartron devices

| *Measurement conditions* | *Values* |
|---|---|
| AC Amplitude (mV) | 10 |
| Initial Frequency (Hz) | $1e^6$ |
| Final Frequency (Hz) | 0.1 (logarithmic scale) |
| Step/Decade Interval (s) | 10 |


**Fig. 13:** Ag/AgCl & graphite electrodes and fuel cell

The conductivity is the capacity a material or substance has in order to allow the electric current flows through it, or what is the same, the capability it has to transport electrons. This value can be altered by many factors such as the temperature, the atomic structures and etcetera. [34]

In order to study the conductivity of every electrolyte and membrane, a correction factor was applied following the formula 4.2, due to every membrane has a different thickness and it affects to the conductivity:

$$F.C. = \frac{r^2 * \pi}{e} \qquad (4.2)$$

Where, "r" is the radius (cm) and "e" is the thickness of the membrane (cm).

In order to analyze the EIS measurements and study the different graphs, Z-view analysis impedance software has been used.

# 4. RESULTS AND DISCUSSIONS

In the next points, the graphs and tables obtained due to the experimental part will be deeply explained and analyzed.

## 4.1 Ionic conductivity of functionalized polysulfones

The conductivity was determined by complex spectroscopy impedance using for the different systems several electrolytes. Moreover, the study was made for many types of proton and anion exchange membranes.

In order to get enough and reliable information, these studies have been done for different membranes, both proton and anion exchange membranes ones and several electrolytes. Therefore, doing in that way we have obtained satisfactory information to compare the conductivities and determine which the most efficient one in those terms is. It is also important to mention that although the Solartron device can measured from frequencies among $10^{-1}$ to $10^{6}$ Hz, the graphs have been represented until the value of $10^{5}$Hz because at high frequencies, the admittance of all the concentrations and electrolytes tends to the same value, what demonstrates that the device has some limitations at these high values, and the conductivity level at that great frequencies is not related with the membrane's impedance.

### 4.1.1 Ionic conductivity of membranes: Effect of the electrolyte concentration

In this point, the admittance in terms of the frequency will be explained. For this experiment, NaCl has been chosen as the electrolyte for the anion exchange membrane study, and HCl for the proton exchange membrane ones. Moreover, in case of the proton exchange membrane, the SPES6 membrane has been used for this experimental part. The ionic conductivity was determined by aqueous solutions at different concentrations.

As we have studied both anion and proton exchange membranes, this item will be also separated into these two.

#### *4.1.1.1 Effect of HCl electrolyte concentration in proton exchange membrane*

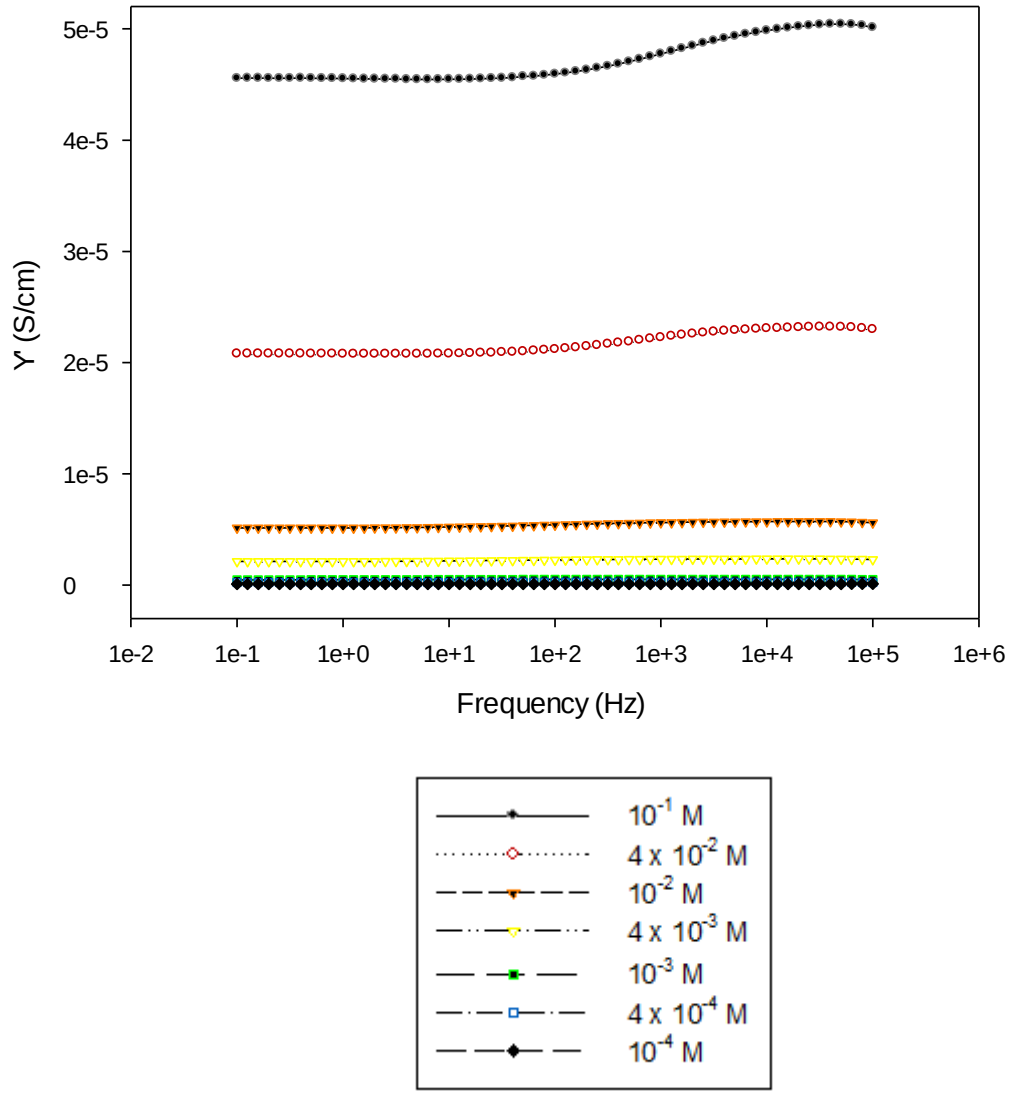


**Fig. 14:** SPES 6 HCl (Y' vs Hz) Bode diagram

As it can be observed on figure 14, where the results of conductivity for membrane SPES 6 at different concentrations for the electrolyte HCl are shown, every concentration output of admittance versus frequency has two distinct curves, being more clearly observed as higher the concentration is, because at minor concentrations the differences between the membrane and the electrolyte are lower due to the value of this one is smaller. These two curves correspond to two different contributions; the first one is associated with the membrane, and the second one with the electrolyte. [33]

Moreover, it is necessary to take into account when analyzing the results that the electrolyte is soaked inside of the membrane, and in general this condition produce that at higher the concentration of the electrolyte greater the admittance. This happens because the membrane moisturize faster as higher the concentration is, what produces greater differences in the measurement between them, and what explains that insignificant distinction among the lower concentrations. The contribution of the electrolyte to the membrane is the variation which is produced in the conductivity when varying the concentration of the electrolyte, so that is why when higher the concentration more number of protons can go through the membrane and therefore the conductivity grows. Another important aspect is that the maximum concentration the membrane is going to reach is marked by the conductivity of the electrolyte.

Although five hours before the measurements were taken the membrane was moved from a concentration of $1M$ to $10^{-4}M$, it only lasted six minutes between every concentration measurement, what provoked that at the lowest concentration, the membrane had not enough time to hydrate properly and so that is why the admittance outputs obtained at these levels are very similar. Therefore, as it can be observed on the previous diagram, the values from $10^{-4}\ M$ to $10^{-3}M$ have less difference than the rest.

#### *4.1.1.2 Effect of NaCl electrolyte concentration in anion exchange membranes*

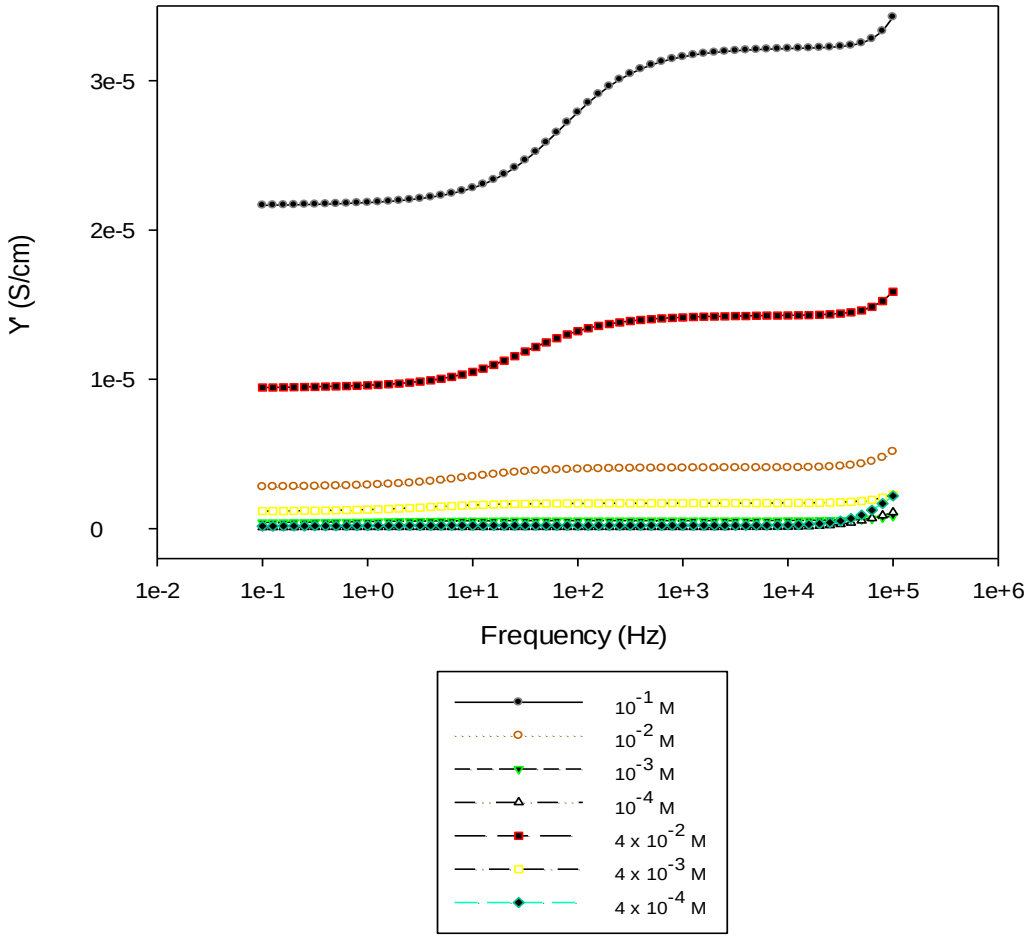


**Fig. 15:** Anion exchange membrane NaCl (Y' vs Hz) Bode diagram

In this figure 15, the results of the admittance versus the frequency are shown for the anion exchange membrane varying the concentrations of the electrolyte NaCl. The explanation on the difference of the value of the admittance for every concentration and the hydration of the membrane are the same as in the proton exchange membrane case, but it is important to stand out that the values of the conductivity in this graph are lower than the values of the previous one (figure 14). The reason of this difference it is because the $H^+$ (proton that is moving from anode to cathode in proton exchange membrane fuel cells) is smaller than the $OH^-$ (anion that is moving in anion exchange membrane fuel cells), or $Cl^-$ in this case, and this characteristic allows it to move faster through the fuel cell, what produce a higher conductivity. In this case, the two curves that were mentioned in the previous point 4.1.1.1, can be more clearly observed because

the contribution of NaCl is lower than the HCl, and that creates more differences among the value of the membrane and electrolyte conductivity.

Among the frequencies of $10^1$ and $10^3$ Hz it can be observed a steeper curve with a significant variation of the admittance with respect to the frequency. It is because between these two points there are several contributions in the system and, due to that reason, the conductivity varies widely in this range of frequencies. Then, it established up to $10^5 Hz$, point at which all the concentrations tends to the same value, because the velocity is so high that the membrane's impedance is almost negligible for all of them.

### 4.1.2 Ionic conductivity of membranes: Aqueous solutions

#### *4.1.2.1 Nyquist graph at $10^{-2}$ M for HCl and NaCl electrolytes*

Nyquist diagram compare the real impedance (Z') with the imaginary one (Z"). In the figures 16 and 17 we have obtained two semicircles, being the first one, high frequency arc (HFA), related with the capacitance of the membrane, and the second and the deformed one, low frequency arc (LFA), with the interphase between the membrane and the diffusion of the electrolyte. [33]

In all the cases that are going to be shown on the next lines, the high frequency semicircle does not intercept the origin, what means there is a resistive element in series with the other two processes and it is related with the electrolyte.

The curves start at the frequency $1e^{+5}$ because in addition to the contribution of the capacitance of the membrane and the interphase among the membrane and the electrolyte, there is also a contribution by the diffusion of the electrolyte for lower frequencies. But in this case it doesn't appear because it has not resistive element. [35]

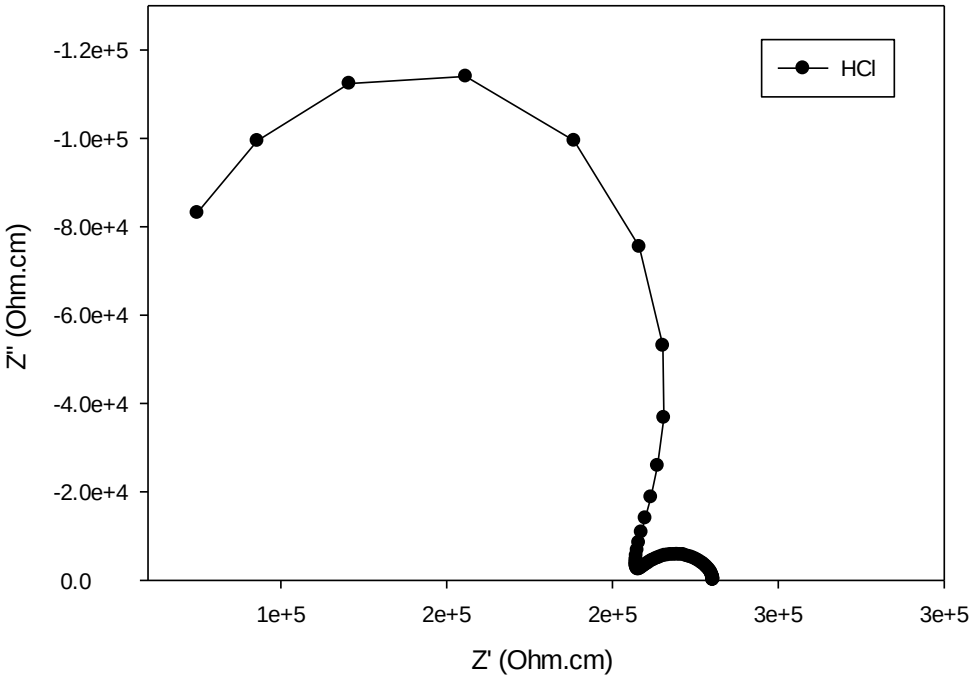


**Fig. 16:** SPES 6 HCl (Z'' vs Z') $10^{-2}M$ Nyquist diagram

According to the figure 16, we can conclude that the higher resistivity is the one shown by the membrane, being the electrolyte's almost negligible. The shape showed in the case of the second semicircle is due to the interaction between the membrane and the electrolyte.

In the following figure (figure 17) it could be seen how that shape of the interphase's semicircle is bigger and more curved than in the case of HCl, this is because the anion electrolyte conducts less than electrolyte in the proton exchange membrane one, and therefore the impedance is higher than in HCl case producing a lower conductivity.

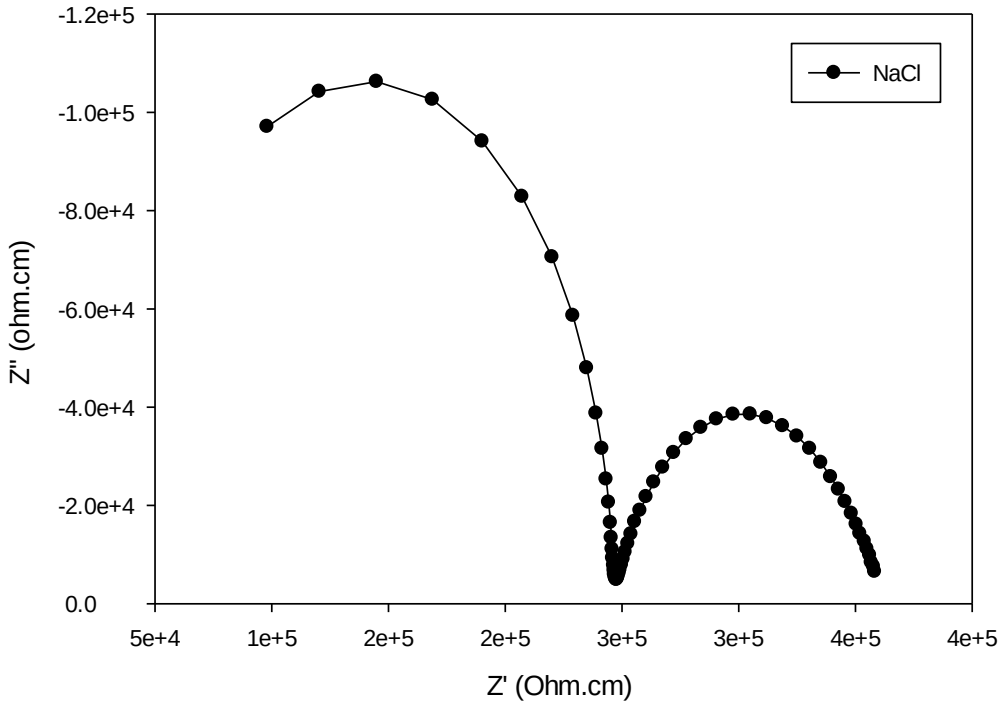


**Fig. 17:** Anion exchange membrane NaCl (Z'' vs Z') $10^{-2}M$ Nyquist diagram

In this case (figure 17), again the membrane has more resistivity than the electrolyte, what is normal due to the membrane has a maximum level of hydration that never is greater than the amount of concentration that the electrolyte has. But in this diagram, the second semicircle is bigger and differently from the previous graph, that represents the interaction among the membrane and the electrolyte is worse and therefore the resistivity is higher and the conductivity lower in comparison with the proton exchange membrane plot (figure 16).

Although we can conclude that the second semicircle, the one that represents the diffusion of the electrolyte, of the NaCl is bigger than the one of the HCl, the resistivity is greater at the anion electrolyte, what produce a lower conductivity. And that result has sense, due to the ion $Na^+$ is bigger than the $H^+$, and so that is why it moves slower and the conductivity is lower. [31]

#### *4.1.2.2 Nyquist diagram comparison at $10^{-2}$ & $4 \times 10^{-2}$ M for HCl and NaCl electrolytes*

In the figure 18 and 19 it could be observed, by a Nyquist diagram, how the concentration of the electrolyte can affect the electrochemical properties of the membrane due to the interaction between them. This comparison has been done for two intermediate concentrations.

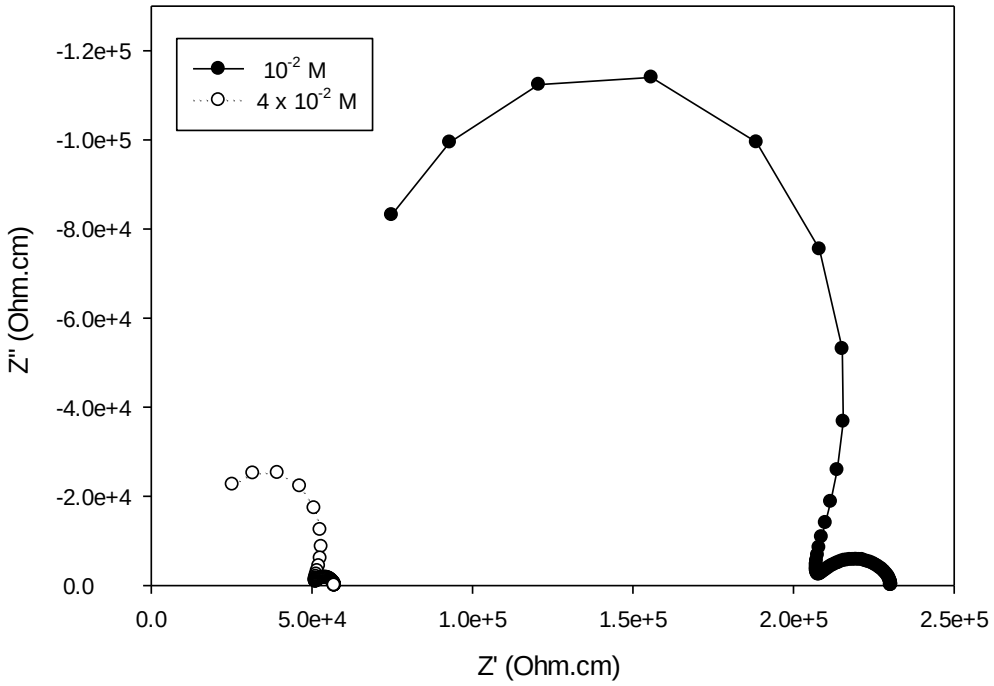


**Fig. 18:** SPES 6 HCl (Z'' vs Z') $10^{-2}$ & $4 \times 10^{-2} M$ Nyquist diagram

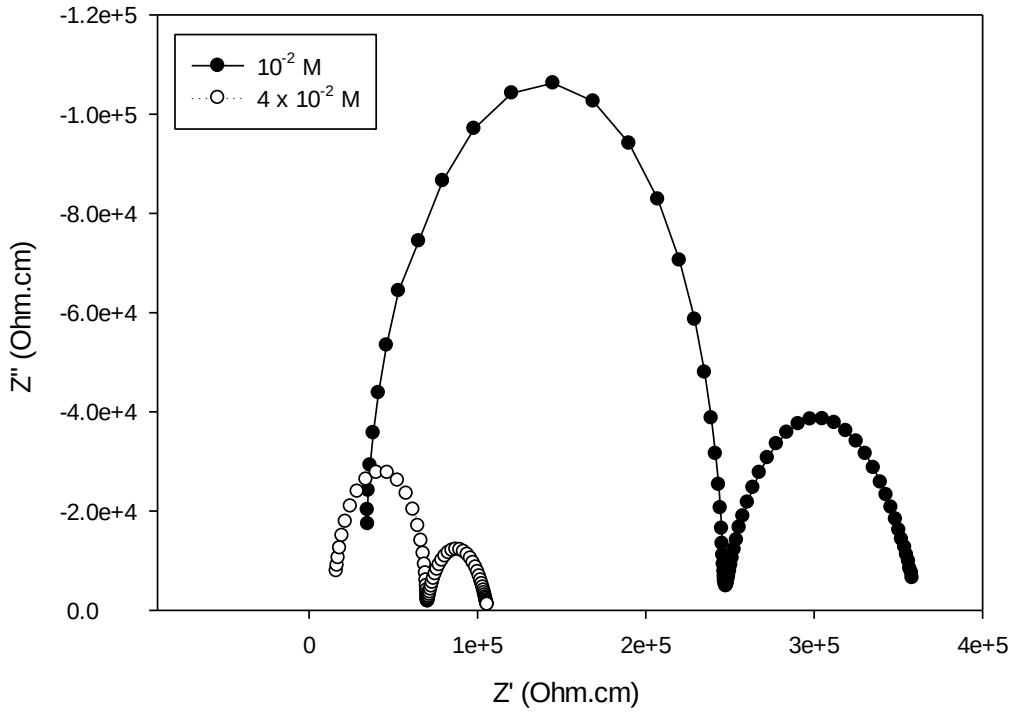


**Fig. 19:** Anion exchange membrane NaCl (Z" vs Z') $10^{-2}$ & $4 \times 10^{-2} M$ Nyquist diagram

In these Nyquist diagrams (figure 18 and 19) for a proton and anion electrolyte, respectively it can be observed that at higher the concentration, lower the resistivity at the diffusion of the electrolyte, obviously this situation takes place because when the amount of protons $H^+$ or anions $Cl^-$ is greater, the conductivity also increases and that reduces the resistivity.

It is also important to stand out that the resistivity of one membrane is lower than of the another, that happens because as the electrolyte is embedded in the membrane, as higher the concentration, greater will be the ionic conductivity of the membrane, and in this diagram the result properly shows that at $4 \times 10^{-2} M$ the membrane has less resistivity than at $10^{-2} M$ because its hydration is higher.

As we have observed on the previous comparison, made on the point 4.1.2.1, the anion exchange membrane electrolyte has a greater low frequency arc, making worse interaction among the membrane and the electrolyte, but also enhancing the resistivity, what explains the lower conductivity in comparison with the proton exchange membrane ones.

#### *4.1.2.3 Proton exchange membranes comparison for $4 \times 10^{-4}$ M electrolytes concentration*

In one of the previous points, 4.1.1.1, it has been analyzed how the admittance level varies depending on the concentration of HCl and the frequency. In this case, it is going to be study for the same concentration, $4 \times 10^{-4} M$, the variation of admittance in terms of the proton exchange membranes, SPES 3, 6 and 9. It can also be compared the most conductive electrolyte for the same concentration and the three different proton exchange membranes.

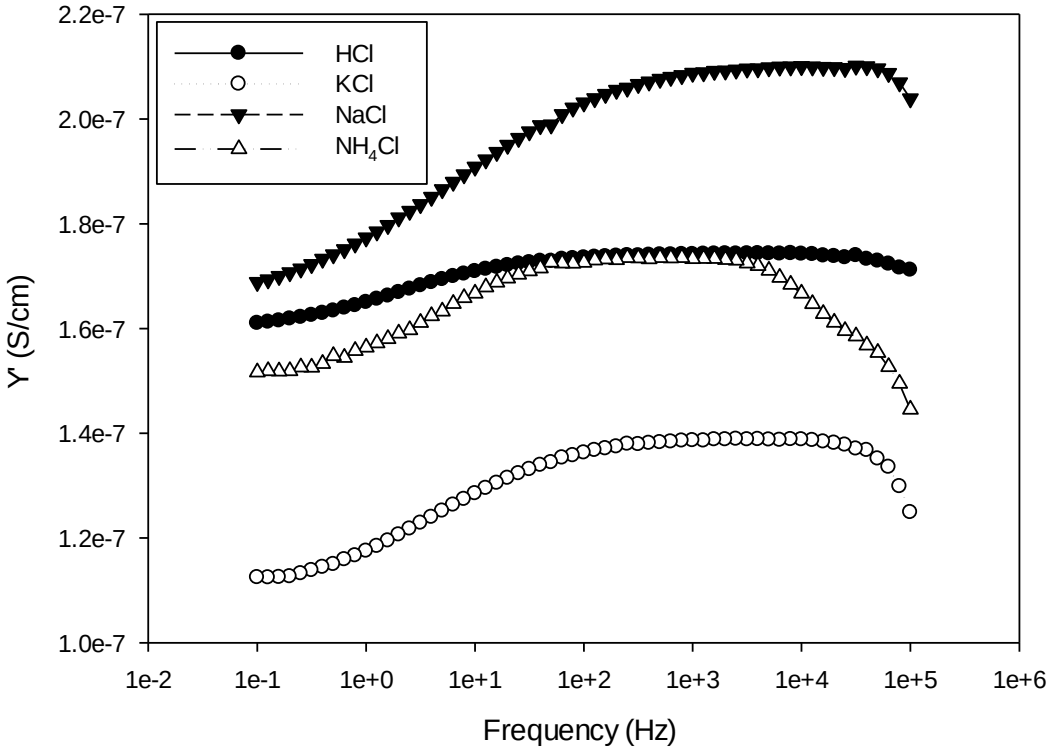


**Fig. 20:** SPES 3 (Y' vs Hz) $4 \times 10^{-4} M$ Bode diagram

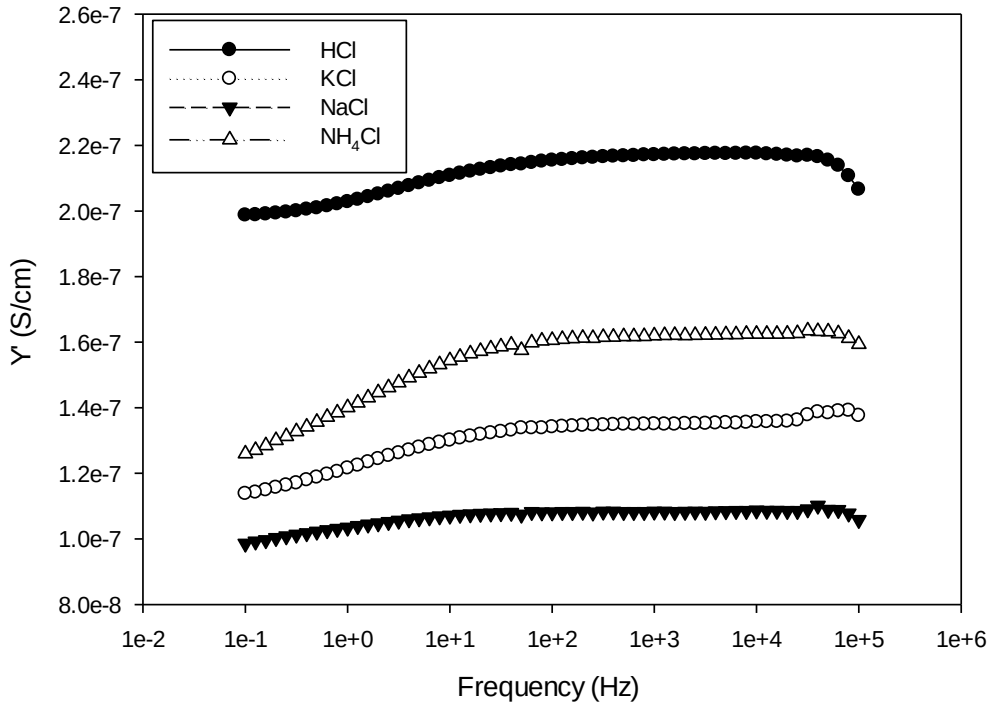


**Fig. 21:** SPES 6 (Y' vs Hz) $4 \times 10^{-4} M$ Bode diagram

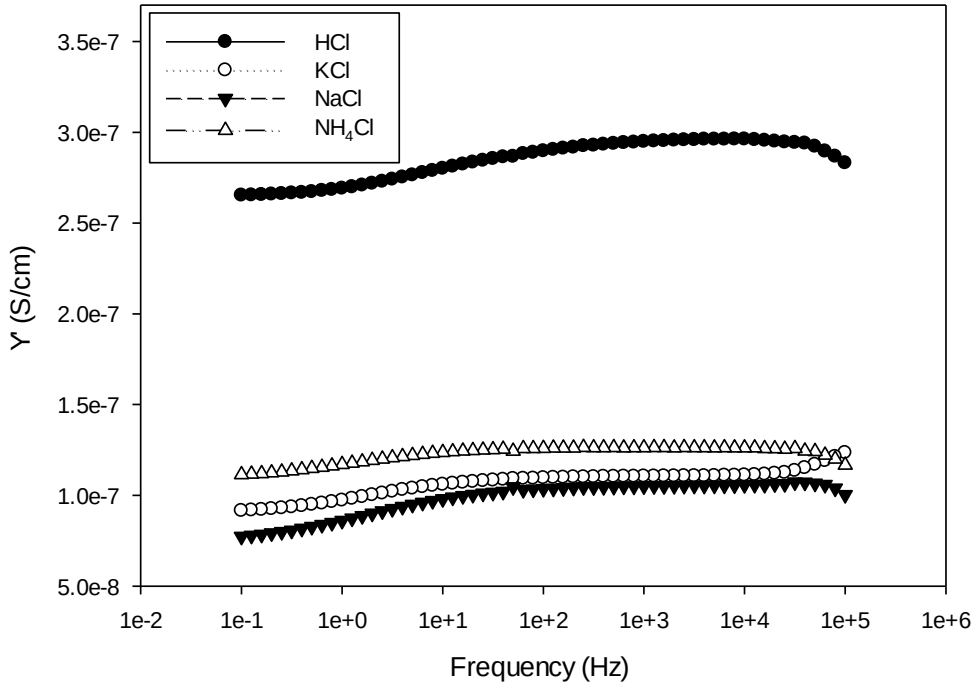


**Fig. 22:** SPES 9 (Y' vs Hz) $4 \times 10^{-4} M$ Bode diagram

In accordance with the three previous figures 20, 21 and 22, Bode diagrams, for the membranes SPES 3, 6 and 9 respectively, we can conclude that i) First of all, talking about ion mobility, we can observe on the graphs that the conductivity follows this tendency: $> NH_4Cl > KCl > NaCl$ . ii) What has sense if we take into account that the cation mobility in water at 298K is $36.23 \times 10^{-8} \frac{m^2}{V*s}$ for the $H^+$, $7.62 \times 10^{-8} \frac{m^2}{V*s}$ for the $NH_4^+$ and for the $K^+$ and $5.19 \times 10^{-8} \frac{m^2}{V*s}$ for the $Na^+$. iii) In the case of the SPES 3 graph membrane, we could observe NaCl is the one with the higher conductivity. This happens because the thickness of the membrane plays also an important role when talking about conductivity, as it can be observed in table 3. [31]

Secondly, it is very important to study the ion transport, which can be described by two different mechanisms: Grotthus and Vehicular mechanism. The first one, take into account the protons moving through the membrane by hydrogen chains from an acid side (sulfonic groups surrounded by water molecules) to the next one. In order to produce this mechanism, high activation energy is needed due to the formation and breaking hydrogen chains (Ea among $14 - 40 \frac{kJ}{mol}$ ). The vehicular mechanism instead, is characterized for having low activation energy in compare with the Grotthuss mechanism, and it is produced by the proton's diffusion along with the water molecules forming compounds such as $H_3O^+ \, or \, H_5O_2^+$. In the case of proton exchange membrane fuel cells, normally, low activation energy is needed to move the protons through the membrane. Therefore, vehicular mechanism is often the one applied in this kind of fuel cells. [9]

Another important aspect is the amount of sulfonating agent added to prepare the membranes. The differences between the membrane SPES 3, 6 and 9 respectively is the amount of these sulfonating agent or, what is the same, the amount of functional groups, being the membrane SPES 9 the one with more and the SPES 3 the one with less. This number of functional groups has a direct relationship with the conductivity of the membrane, when the amount of functional groups in the polymer increase, the conductivity too. Following this relationship, membrane SPES 9 will conduct more than SPES 6 that, at the same time, will conduct more than SPES 3. But this is not the only aspect has to be taken into account when talking about the conductivity, the thickness of the membrane is also very important, when thicker it is, greater is the conductivity. Big differences on it can completely change the order of conductivity defined by the amount functional groups. If we look at the following table (table 3), we can observed that for example in the case of SPES 3 membrane, although the $H^+$ has a higher cation mobility than the $Na^+$and the protons move faster producing a greater conductivity in the first one than in the second one, the different in thickness among this two membranes is so huge that for SPES 3 membrane, if we look at the diagram 20, NaCl conducts more than HCl. Then, according to the figure 22, it can be observed that for SPES 9 the cation mobility and the thickness of the membrane for HCl is greater than the rest, and so that is why it is the electrolyte with the highest conductivity among these four.

**Table 3.** Proton exchange membrane thickness

| Membrane/ Electrolyte | $HCl$ thickness ($\mu m$) | $NH_4Cl$ thickness ($\mu m$) | $KCl$ thickness ($\mu m$) | $NaCl$ thickness ($\mu m$) |
|---|---|---|---|---|
| SPES 3 | 42.00 | 51.60 | 73.20 | 72.75 |
| SPES 6 | 61.00 | 87.80 | 89.00 | 93.00 |
| SPES 9 | 75.50 | 69.40 | 67.40 | 64.83 |

#### *4.1.2.4 Anion exchange membrane electrolyte comparison for $4 \times 10^{-4}$ M concentration*

The diagram 23 follows the same study as the proton exchange membrane ones. In the case of anion exchange membrane, the anion mobility of the $OH^-$ is much greater than $Cl^-$. Therefore, $KOH$ conducts more than $KCl$. Another important aspect that, as in the proton exchange membrane case, is important to stand out, is the thickness of the membrane.

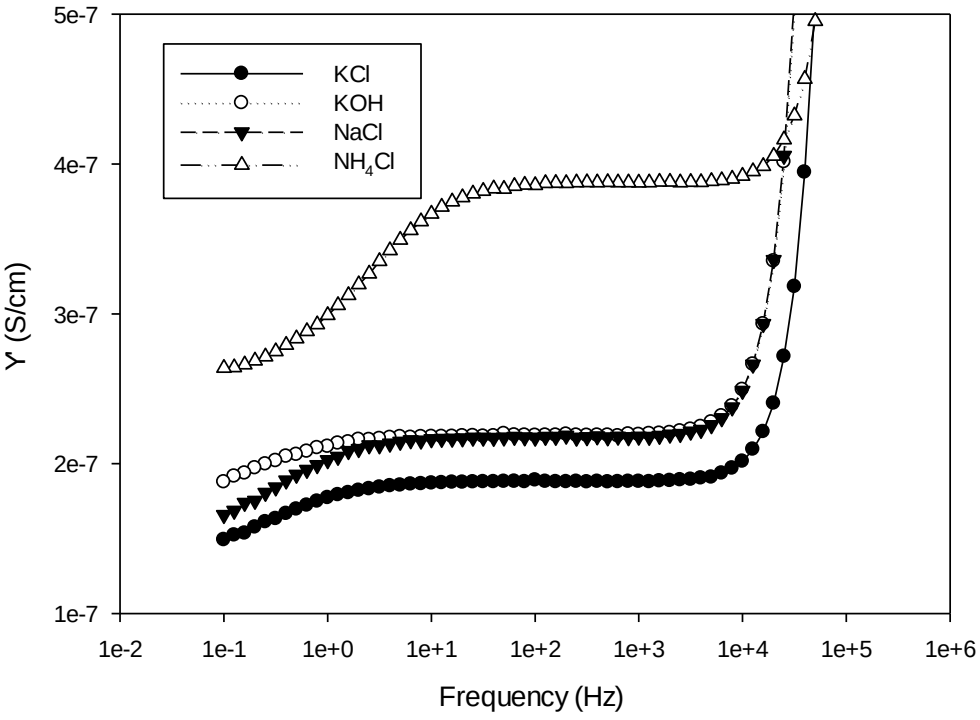


**Fig. 23:** Anion exchange membrane (Y' vs Hz) $4 \times 10^{-4} M$ Bode diagram

As it can be observed in the next table (table 4), although the anion mobility is the same for $NaCl$ and $KCl$ compounds, the thickness of the first one is bigger than the second one.

The huge increase on the admittance in the frequency range from $1e^{+4}$ to $1e^{+5}$ Hz is because at those values the measurement device has some limitations that don't allow getting good results and so that is why the admittance for all the electrolytes tends to the same values.

**Table 4.** Anion exchange membrane thickness

| Membrane/ Electrolyte | $KCl$ thickness ($\mu m$) | $KOH$ thickness ($\mu m$) | $NaCl$ thickness ($\mu m$) | $NH_4Cl$ thickness ($\mu m$) |
|---|---|---|---|---|
| Anion exchange membrane | 132.2 | 134.4 | 171 | 130 |

#### *4.1.2.5 Nyquist's proton exchange membrane diagrams comparison HCl among SPES 3, 6 & 9 for $10^{-2}$ M*

In the Nyquist diagram obtained, the first semicircle, or high frequency arc (HFA), has direct relation with the capacitance of the membrane. So that is why, observing the figure 24 it is very clear to differentiate that the one with the highest resistivity is SPES 3, followed by the SPES 6, and the one with the lowest resistivity is SPES 9. This happens because, as mentioned in the previous point, when more number of functional groups a membrane has, greater the conductivity in it. Therefore, as the SPES 9 is the one with the greater amount of functional numbers, it is the membrane with the highest conductivity and at the same time with the lowest resistivity. It is that the reason why, it has the smallest curve at the first semicircle, HFA.

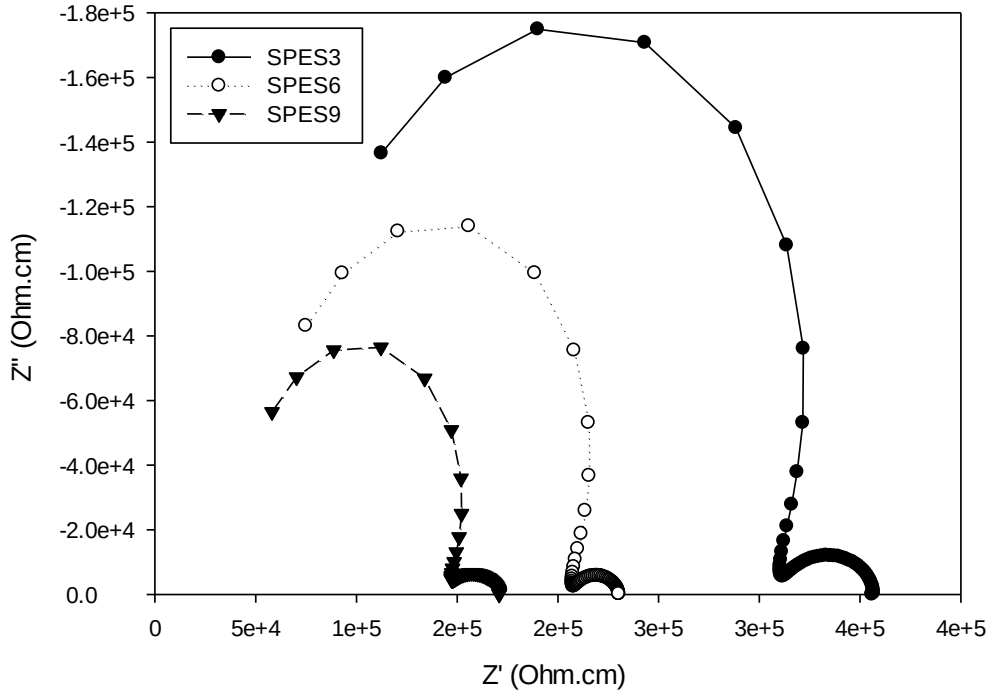


**Fig. 24:** SPES 3, 6 & 9 HCl (Z" vs Z') $\mathbf{10^{-2}}M$ Nyquist diagram

If we now focus on the second semicircle, low frequency arc (LFA), that has relation with the interphase between the electrolytes and the membranes, we can see that the contribution of the electrolyte's diffusion is very important reducing significantly the value of the resistivity, but the contribution of the membrane is still kept during the interphase, and due to that reason the second arc of the SPES 3 membrane is the biggest one in comparison with SPES 6 and 9.

#### *4.1.2.6 Electrolyte resistivity comparison for proton exchange membrane SPES 6 at* $\mathbf{4 \times 10^{-4}}M$

In the figure 25, depending the range frequency, the graph is divided in three parts: From $1\,Hz$ to $10\,Hz$, belongs to the interphase among the membrane and the electrolyte, from $10\,Hz$ to $10^3\,Hz$ the capacitance of the membrane is represented and from $10^3\,Hz$ to $10^5\,Hz$ the diffusion of the electrolyte is shown. [33]

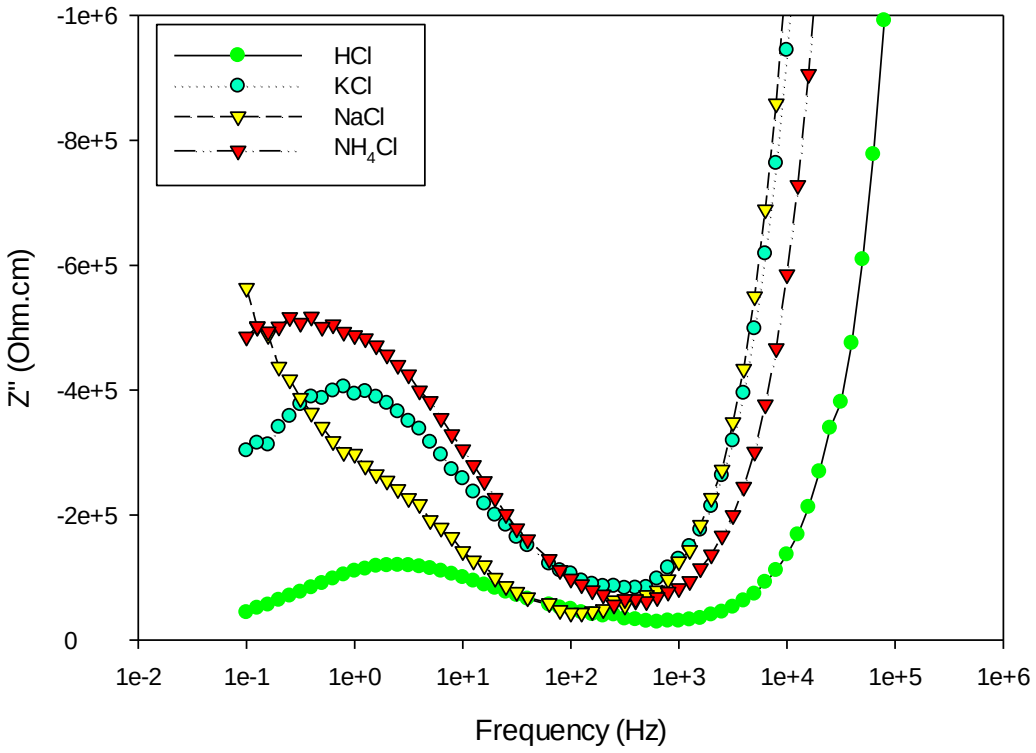


**Fig. 25:** SPES 6 (Z" vs Hz) $4 \times 10^{-4} M$ Nyquist diagram

From the interphase among the membrane and the electrolyte, we can check that the effect of the membrane contribution is very big in comparison with the diffusion of the electrolyte because the value of the resistivity decreases when the only contribution is the one of the membrane.

At the diffusion of the electrolyte phase, the electrolyte with the less resistivity means it has the highest conductivity and it has sense taking into account the cation mobility is the following: $HCl > NH_4Cl > KCl > NaCl$. [31]

From the frequency of $10^5\ Hz$ in advance, the values of the resistivity are not associated with the impedance of the membrane and all the electrolytes have tendency for the same value, because the measurement device has some limitations as such as big frequencies.

#### *4.1.2.7 Electrolyte resistivity comparison for anion exchange membrane at $4 \times 10^{-4}$ M*

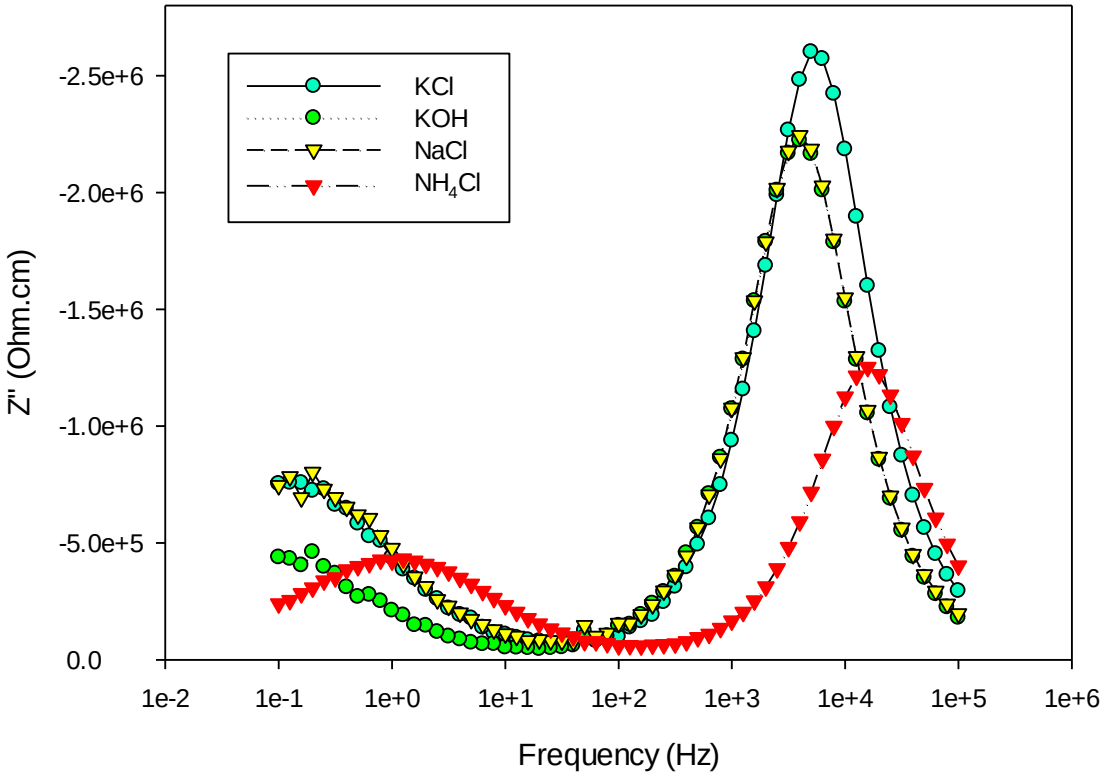


**Fig. 26:** Anion exchange membrane ($Z$" vs Hz) $4 \times 10^{-4} M$ Nyquist diagram

The figure 26 follows the same study as the previous proton exchange membrane case (diagram 25 and 26). It is also divided by three different parts: From 1 $Hz$ to 10 $Hz$, belongs to the interphase among the membrane and the electrolyte solution, from 10 $Hz$ to $10^3$ $Hz$ the capacitance of the membrane is represented and from $10^3$ $Hz$ to $10^5$ $Hz$ the diffusion of the electrolyte is shown. [33]

It can be also seen the importance of the contribution of the membrane when reducing the resistivity of the system.

Another important aspect is the difference between the resistivity of the AEM and PEM. As it can be observed, the value of the AEM is greater, what has sense taking into account the AEM conducts less than the proton exchange membrane one. And this decrease in the conductivity implies an increase in the resistivity.

#### *4.1.2.8 Nyquist's AEM and PEM diagrams comparison for $4 \times 10^{-4}$ M*

In the diagram 27, as in the previous Nyquist's cases, the first arc (HFA) corresponds to the membrane contribution, while the second one (LFA) with the interphase between the membrane and the electrolyte. [33]

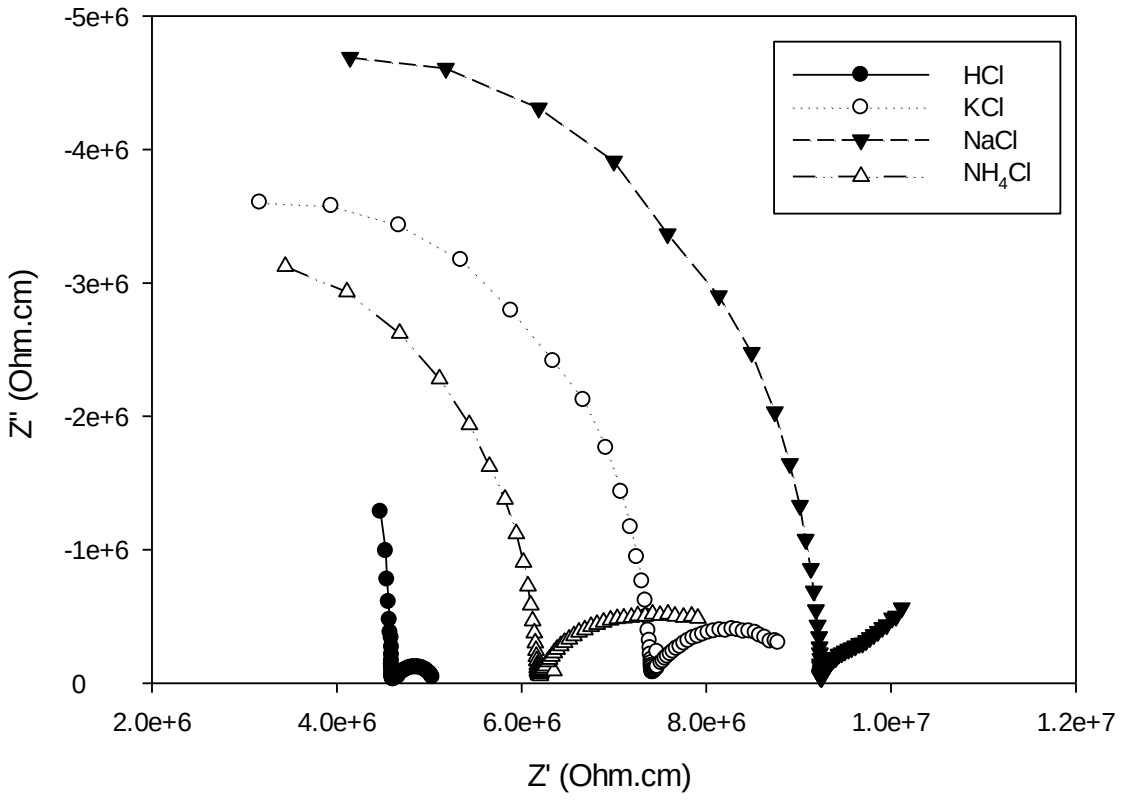


**Fig. 27:** SPES 6 (Z" vs Z') $4 \times 10^{-4} M$ Nyquist diagram

As it can be observed, if we compare this graph with the one of the conductivity (figure 21), as lower it is higher is the resistivity. Therefore, if in the conductivity graph, following the cation mobility, the order was: $HCl > NH_4Cl > KCl > NaCl$, here it will be the other way around: $NaCl > KCl > NH_4Cl > HCl$. [31]

Looking at the second arc of the graph, the highest contribution of the electrolyte solution is in the case of the $HCl$, because when checking the interphase among the membrane and the electrolyte is the one with the lower resistivity what represents it makes the best contribution in compare with the rest of the electrolytes. For the $KCl$ *and* $NH_4Cl$ the interphase is very similar, being the worst the $NaCl$ interphase.

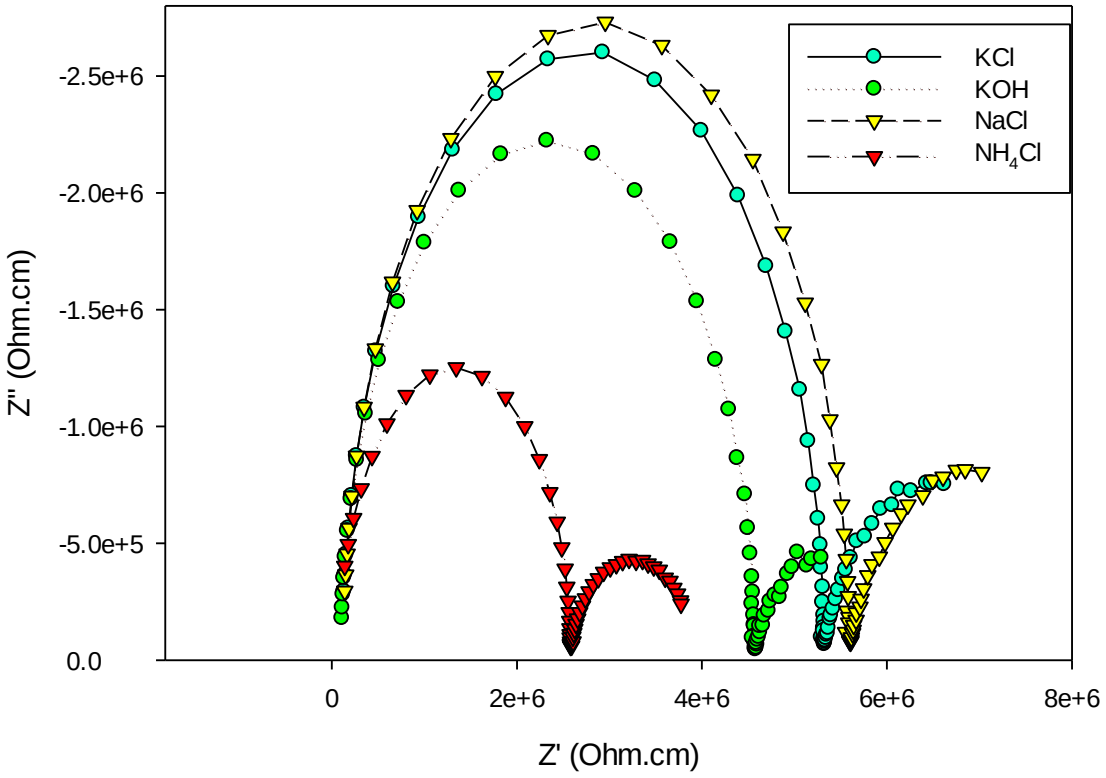


**Fig. 28:** Anion exchange membrane (Z" vs Z') $4 \times 10^{-4} M$ Nyquist diagram

Following the same procedure as in the previous proton exchange membrane, in the diagram 28, the first arc (HFA) corresponds to the membrane contribution, and the second one (LFA) with the interphase between the membrane and the electrolyte.

In this case, the higher electrolyte's contribution is made by the $NH_4Cl$ solution and the worst by the $NaCl$, because it is the one that highest resistivity presents.

### 4.1.3 Ionic conductivity of membranes in aqueous solution of complex salts

In this point, the ionic conductivity of the complex salt $NH_4Cl$ will be studied. In the case of the proton exchange membrane fuel cell, the cation moving will be $NH_4^+$, and in

the case of the anion exchange membrane one, the anion moving will be $Cl^-$. In terms of ionic mobility, both compounds have a similar value, what will be observed in the following graphs, because the outputs regarding these values will be very similar.

#### *4.1.3.1 Ionic admittance comparison $NH_4Cl$ (Y' vs Hz)*

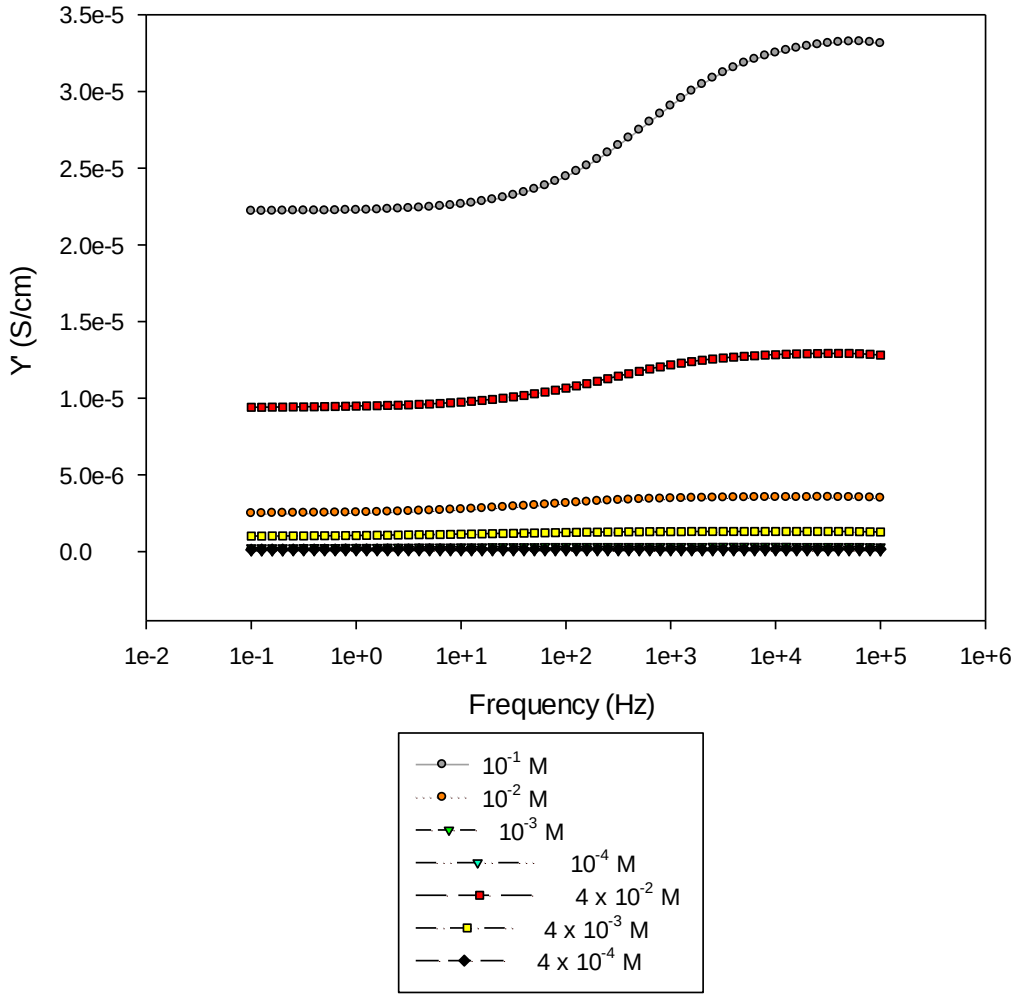


**Fig. 29:** SPES 6 $NH_4Cl$ (Y' vs Hz) Bode diagram

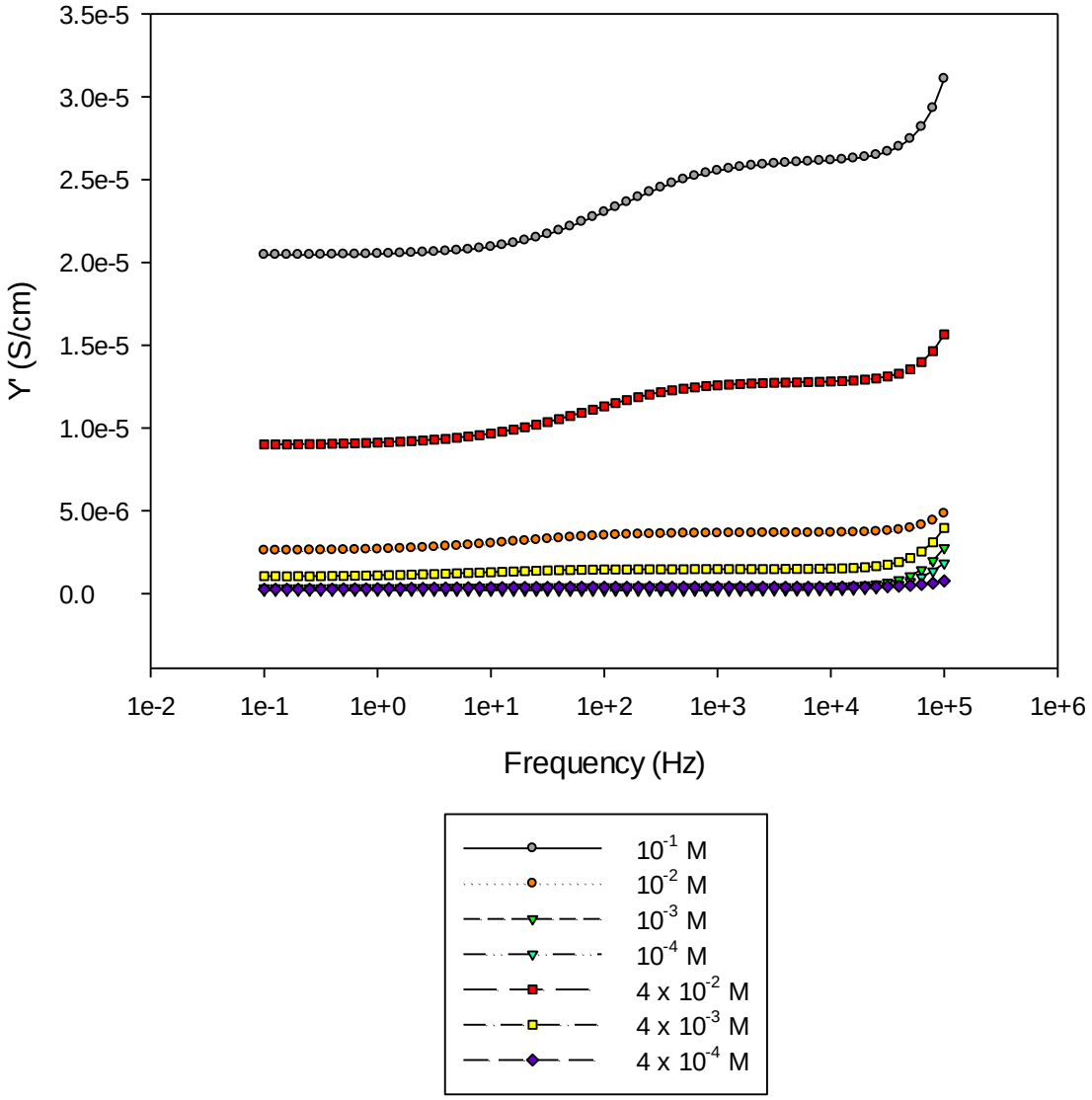


**Fig. 30:** Anion exchange membrane $NH_4Cl$ (Y' vs Hz) Bode diagram

For both previous diagrams (figure 29 and 30), it can be checked that higher the concentration of the electrolyte solution, greater the conductivity. This happens because the amount of cations or anions moving respectively, depending which ionic fuel cell we are studying, are higher when the concentration of the electrolyte solution does.

It can be also observed that when greater the concentrations more distance from the conductivity value. The reason of that fact is that the time spent between the different measurements is almost the same for all the concentrations. Therefore, if the membrane hydrates from an electrolyte with a high concentration that presents greater conductivity than an electrolyte with lower concentration, the membrane will also conduct more.

That produce the last ones does not have several differences between them because as they have so low concentrations with small differences, the conductivity of the membrane is also very similar and that produces that the values of admittance are almost equal.

Another important aspect that has been shown previously (figures 29 and 30), it is that differently from the normal salts, where the proton electrolyte solution shows a higher conductivity than the anion electrolyte solution ones, in this case as the ionic mobility is very similar among $NH_4^+ \; and \; Cl^-$, the dissociation is very similar between them. And in accordance with the values obtained, they are very high values.

#### *4.1.3.2 Ionic resistivity comparison $NH_4Cl$ (Z" vs Z') at $10^{-3}M$*

For the complex salts (figures 31 and 32), as in the previous Nyquist's cases, the first semicircle, high-frequency arc (HFA), corresponds to the membrane contribution, while the second one, low-frequency arc (LFA), with the interphase between the membrane and the electrolyte solution.

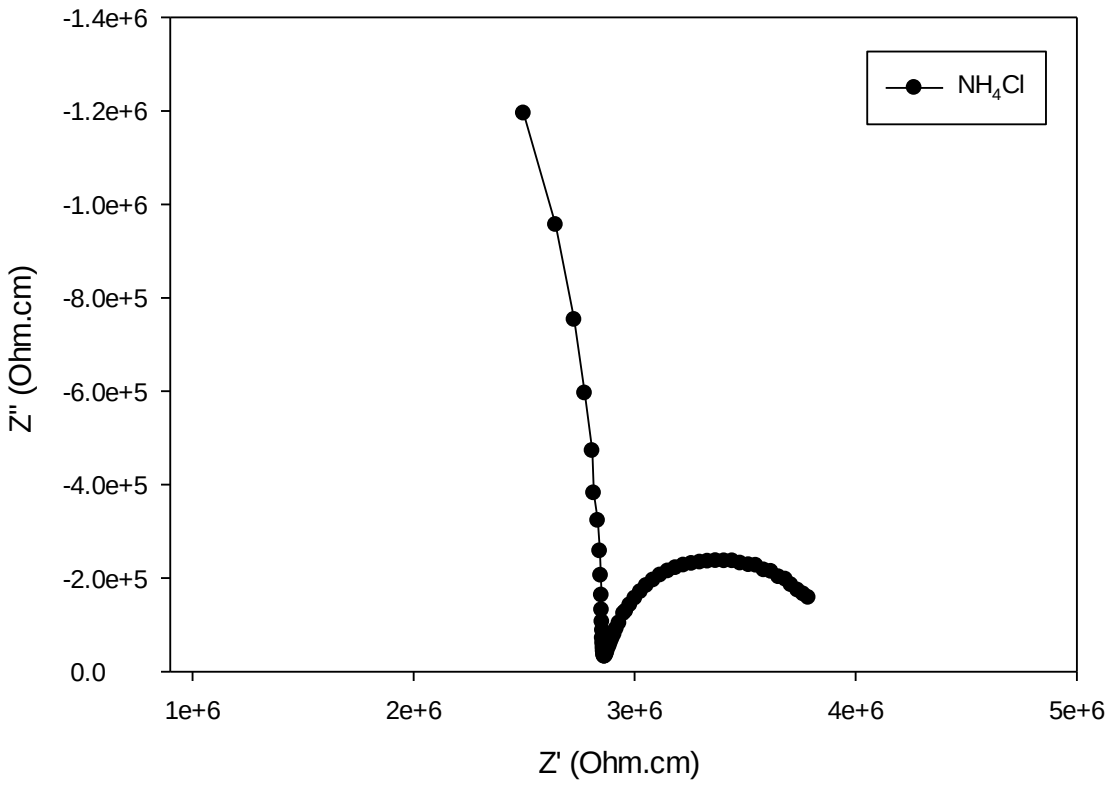


**Fig. 31:** SPES 6 $NH_4Cl$ (Z" vs Z') $10^{-3}M$ Nyquist diagram

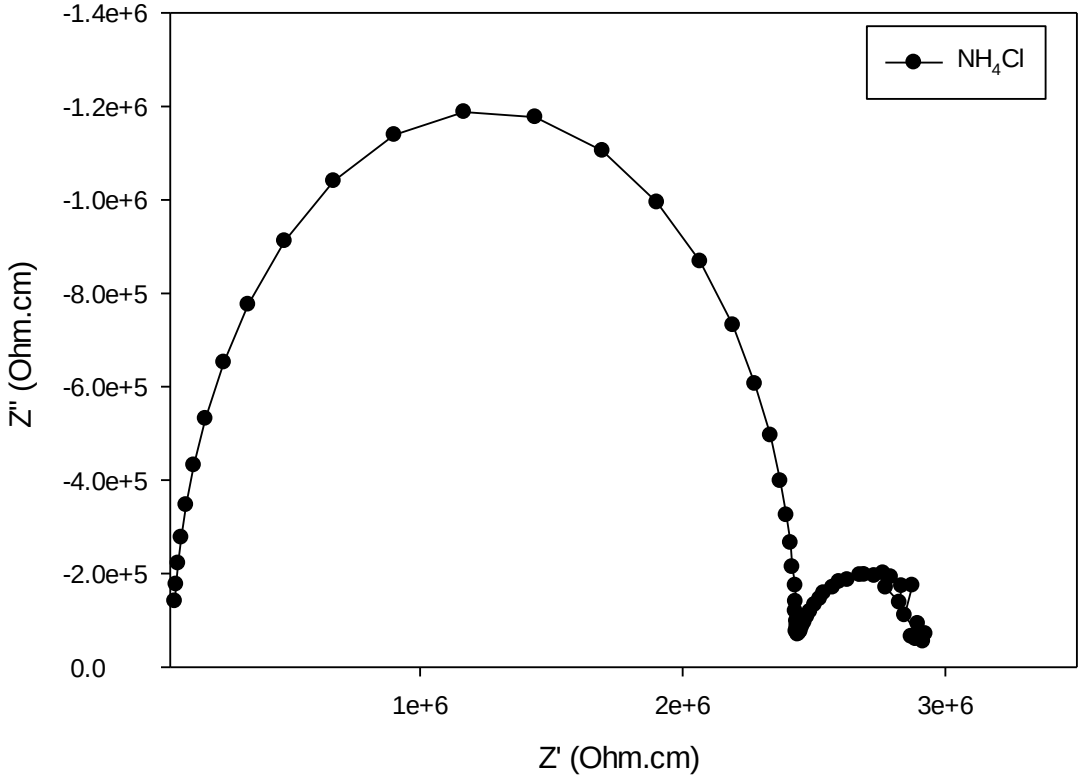


**Fig. 32:** Anion exchange membrane $NH_4Cl$ (Z" vs Z') $10^{-3}M$ Nyquist diagram

In both cases we can see that the capacitance of the membranes are very similar, and the diffusion of the electrolyte solution when talking about the interphase between the membrane and the electrolyte too.

This explains why the values of the admittance in the previous diagrams (figure 29 and 30) are very similar.

# 5. SOCIO-ECONOMIC FACTORS

## 5.1 Budget

The budget of this research project was made taking into account the cost of the materials and characterization techniques used. All this is detailed in table 5.

**Table 5.** Budget of the project

| Reagents | | | | |
|---|---|---|---|---|
| Item | Units | Description | Unit Price | Total Price |
| 1.1 | 1 | Pack size 25g 4,4′-Difluoro-diphenylsulfone | 72.40 | 72.40 |
| 1.2 | 1 | Pack size 250g 4,4'-Isopropylidenediphenol | 14.50 | 14.50 |
| 1.3 | 1 | Pack size 25g 4,4'-Dihydroxybiphenyl | 50.40 | 50.40 |
| 1.4 | 1 | Pack size 250g 4,4'-Dihydroxydiphenylsulfone | 40.00 | 40.00 |
| 1.5 | 1 | Pack size 1L N,N-Dimethylacetamide | 116.00 | 116.00 |
| 1.6 | 1 | Pack size 500g Potassium carbonate | 38.00 | 38.00 |
| 1.7 | 1 | Pack size 50 mL Trimethylsilyl chlorosulfonate | 50.50 | 50.50 |
| 1.8 | 1 | Pack size 1L 1,2-Dichloroethane | 63.00 | 63.00 |
| 1.9 | 1 | Pack size1L Toluene | 38.75 | 38.75 |
| 1.10 | 1 | Pack size 100g Polysulfone | 117.50 | 117.50 |
| 1.11 | 1 | Pack size 100mL Tin (IV) chloride | 31.70 | 31.70 |
| 1.12 | 1 | Pack size 100mL Chlorotrimethylsilane | 39.10 | 39.10 |
| 1.13 | 1 | Pack size 1L 1-Methyl-2-pyrrolidone | 97.50 | 97.50 |
| 1.14 | 1 | Pack size 25mL N, N, N′, N′-tetramethylethylenediamine | 20.50 | 20.50 |
| 1.15 | 1 | Pack size 500mL Trimethylamine solution | 29.00 | 29.00 |
| 1.16 | 1 | Pack size 1L Hydrochloric acid | 19.50 | 19.50 |
| 1.17 | 1 | Pack size 500g Potassium hydroxide | 67.00 | 67.00 |
| 1.18 | 1 | Pack size 500g Potassium chloride | 38.25 | 38.25 |
| 1.19 | 1 | Pack size 1Kg Sodium chloride | 27.75 | 27.75 |
| 1.20 | 1 | Pack size 500g Ammonium chloride | 26.50 | 26.50 |
| Total reagents | | | | 997.85 |

| Characterization techniques | | | | |
|---|---|---|---|---|
| Item | Units | Description | Unit Price | Total Price |
| 2.1 | 16 | Electrochemical Impedance Spectroscopy measurement | 40.00 | 640.00 |
| Total characterization techniques | | | | 640.00 |

As summary, the total budget of the project was 1637.85 €.

The gross salary per month is 1,687.02€, but taking into account the days worked at the laboratory were 16 days and 4 hours per day, the amount of money earned per day for a part-time employment is 28.12€, so that is why the total gross salary for the 16 days is 449.87€. [36] But as this work is academicals, the previous amount of money of 449.87€ has not been included in the final budget.

## 5.2 Socio-economic impact

Since some decades ago, it has increased the number of researches focused on finding out sustainable ways to obtain energy. These investigations are producing that the traditional energy systems are being substituted by the new renewable systems.

One of these new energy sources is the so called Fuel Cells, what is based in the utilization of hydrogen to obtain electric and thermal energy. The benefits this energy source has in comparison with other such as Fossil Fuel Cells is that its combustion does not release contaminating gases because it only generates water, and it is an inexhaustible resource due to the necessary fuel (hydrogen) can be obtained from both renewable and non-renewable ways. Therefore, the applications of new energy sources like fuel cells help to reduce the $CO_2$ emissions, particulate matter that is contaminating the air and it does not produce noise pollution due to it does not make any sound. [37]

Another important aspect is that in the conventional energy processes, the chemical energy of the fuel is firstly transform into thermal energy of a fluid, afterwards in mechanical energy and finally in electric energy, following four different transformations. On the other hand, the fuel cells transform directly the chemical energy into the electric one without intermediate conversions. This characteristic allows the fuel cells to have higher efficiency, in transportation and generation of energy, than other conversion energy technologies such as combustion engines or turbines. [38]

In economic terms, as the maintenance cost is minimal in comparison with the conventional energy sources, the only important investment it is necessary to do is the initial installation of hydrogen tanks, for instance in the oil stations if it is used in transportation, and the security facility due to the hydrogen in contact with oxygen (air) can explode. But one this initial investment is done, the maintenance is lower and the useful life longer than most of the energy sources.

# 6. REGULATORY FRAMEWORK

Although the fuel cells are one of the less polluting energy sources, they have to satisfy the Kyoto and Paris agreement, where the amount of gas emissions for the following years was established.

Kyoto Protocol was an International agreement with the objective of reducing the emissions of six gases of greenhouse effect: carbon dioxide ($CO_2$), methane gas ($CH_4$), nitrous oxide ($N_2O$) and three fluorinated greenhouse gases (hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride) between 2008-2012. In this agreement was fixed the reduction of the emission of this kind of gases as a minimum of 5%. Nowadays, the second period of Kyoto Protocol is in effect until 2020, in order to assure all the countries satisfy these conditions. [39]

Paris agreement was celebrated in 2015, and 195 countries signed an international accord about the climate. The governments agreed to limit the worldwide temperature increasing up to 1.5ºC more, offer to the developing nations an international help to adapt better for this new weather changes, reduce as much as possible the effect of the global warming and the emissions in 2030 at least 40%, and invest for 2020 around 100.000 millions of U.S. dollars ($) for this cause. [40]

# 7. CONCLUSION

In this work, the electrochemical properties of a series of noncommercial PEMFCs and AEMFCs have been successfully studied. Current economic, environmental and efficiency advantages and disadvantages of both have been compared, and also an experimental study has been done. The ionic conductivity of the membranes was determined by means of complex impedance spectroscopy. Firstly, the results in the present work demonstrated the reproducibility of the measurements with this technique. Secondly, different electrolyte solutions were employed in order to study their influence in the system. In all the different electrolyte solutions studied, the effect of the concentration solutions clearly affected to the values of ionic conductivity for the membranes. Furthermore, the results obtained showed that as smaller is the ion size, as higher the dissociation of the ion of the electrolyte solution is and the more functional groups the membrane has, greater is the conductivity, and therefore, higher the efficiency. Thus, higher conductivity value was obtained for the PEMs with a higher number of functional groups (SPES9) in HCl solution (obtaining a value of conductivity of $6.09e^{-5}$ S/cm$^{-1}$) due to the higher ion mobility. Moreover, the rest of the membranes evaluated showed competitive ionic conductivity values. So the membranes can be considered promising solid electrolytes for fuel cell applications.

# 8. FUTURE WORK

In our studies and experimental works, the conductivity of both proton and anion exchange membranes at room temperature with different electrolytes solutions has been measured. In order to obtain these values a cell with electrodes composed of graphite and silver chloride were used.

The future work could be to continue with an experimental study at different temperatures for the same set up we have used in order to calculate the activation energy. Thus, it could be possible to know the transport mechanisms for the ions in the membranes, an essential parameter to evaluate the ionic conductivity. It is supposed that at temperatures higher than the ambient one, the conductivity of the membranes increases obtaining better results.

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